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Treatment Techniques for Controlling Trihalomethanes in Drinking Water

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16. ABSTRACT

In this volume, the authors attempt to bring together information developed over the past 6 years, on all aspects of trihalomethanes as they relate to drinking water.

Section I summarizes with references to the primary literature the discovery of the trihalomethane problem, health and regulatory information. Sections II-V also summarizes the literature regarding key background information necessary for an understanding of approaches to initiating control measures and evaluation of their degree of success. Sections VI-XI attempt to be more complete treatments of their subjects including some previously unpublished in-house USEPA - Drinking Water Research Division (DWRD) research results, and selected references to the primary literature, sufficient to describe the state-of-the-art knowledge of trihalomethane treatment techniques, bacteriologic considerations and economic impact of trihalomethane control strategies. Although the authors and contributors realize that research is continuing on this subject and therefore, new data will be forthcoming, sufficient new information is available at this time to warrant this update of the "Interim Treatment Guide for the Control of Chloroform and Other Trihalomethanes," June 1976 (Unpublished).

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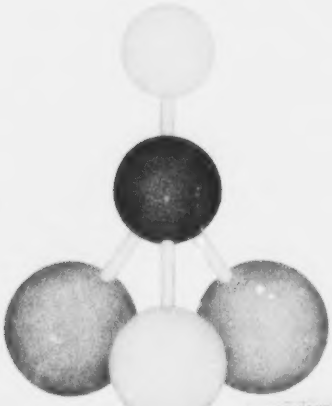

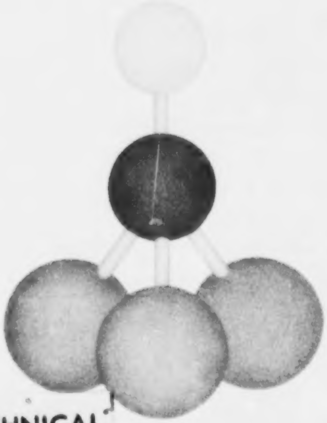

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TREATMENT TECHNIQUES FOR CONTROLLING TRIHALOMETHANES IN DRINKING WATER

by

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

Chloroform and other trihalomethanes are now known to be ubiquitously formed during the chlorination of drinking water. Because of this, intense international research programs have been initiated to study all aspects of this problem. Although research on some aspects continues, sufficient information is now available to warrant compiling resultant data into a single volume. Background information on trihalomethanes in drinking water is summarized with reference citations to the primary literature. Additionally, a state-of-the-art review is given of treatment techniques for trihalomethane control, of control measures on the bacteriologic quality of the treated water, and economic impact of their application.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

PREFACE

In this volume, the authors attempt to bring together information developed over the past 6 years on all aspects of trihalomethanes as they relate to drinking water. The major sections are:

I. Introduction
II. Measurement
III. Mechanism of Formation
IV. Measurement for Treatment Evaluation
V. Examples of Treatment Evaluation Techniques
VI. Treatment Techniques to Remove Trihalomethanes
VII. Treatment Techniques to Remove Trihalomethane Precursors
VIII. Use of Alternative Disinfectants
IX. Maintaining Bacteriologic Quality
X. Treatment Costs
XI. Summary of Treatment Considerations
XII. References
XIII. Appendix

Section I summarizes with references to the primary literature the discovery of the trihalomethane problem, health and regulatory information. Sections II–V also summarize the literature regarding key background information necessary for an understanding of approaches to initiating control measures and evaluation of their degree of success. Sections VI–XI attempt to be more complete treatments of their subjects including some previously unpublished in-house USEPA—Drinking Water Research Division (DWRD) research results, and selected references to the primary literature, sufficient to describe the state-of-the-art knowledge of trihalomethane treatment techniques, bacteriologic considerations and economic impact of trihalomethane control strategies. Although the authors and contributors realize that research is continuing on this subject and, therefore, new data will be forthcoming, sufficient new information is available at this time to warrant this update of the "Interim Treatment Guide for the Control of Chloroform and Other Trihalomethanes" June 1976 (Unpublished).

The authors and contributors hope this compilation of research material will prove useful to those challenged with the responsibility of reducing the trihalomethane content of our Nation's drinking water.

ABSTRACT

In 1974, trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) were discovered to be formed during the disinfection step of drinking water if free chlorine was the disinfectant. Various surveys have shown that this reaction occurs wherever the above conditions are met. This, coupled with the perceived hazard to the consumer's health, led the U.S. Environmental Protection Agency to amend the National Interim Primary Drinking Water Regulations to include a maximum contaminant level of 0.10 mg/L for total trihalomethanes. The Safe Drinking Water Act (Public Law 93-523) requires that every drinking water regulation contain a statement as to what treatment techniques water utilities can employ to achieve compliance with the regulation as well as the maximum contaminant level. This report satisfies the treatment document requirement for the trihalomethane regulation.

Following a general discussion of measurement techniques, mechanisms of formation, and techniques for evaluating treatment, the three approaches for controlling trihalomethanes (removing trihalomethanes, removing trihalomethane precursors, and the use of disinfectants other than free chlorine) are discussed in detail. Finally, a thorough discussion of the impact of trihalomethane control on bacteriologic quality of drinking water and the cost of the various unit processes investigated is contained herein.

For trihalomethane removal, aeration—either by diffused-air or with towers—and adsorption—either by powdered activated carbon or granular activated carbon—is effective. The major disadvantage of this approach is that trihalomethane precursors are not removed by aeration. For trihalomethane precursor control, effective processes are: 1) oxidation by ozone or chlorine dioxide; 2) clarification by coagulation, settling and filtration, precipitative softening, or direct filtration; or 3) adsorption by powdered activated carbon or granular activated carbon. In addition, some modest removal or destruction of trihalomethane precursors can be achieved by oxidation with potassium permanganate, lowering the pH, or moving the point of chlorination to the clarified water. Further, the utility's source should be examined to determine whether or not it can be improved to contain less trihalomethane precursor. Lowering of trihalomethane precursor concentrations has the additional advantage of reducing overall disinfectant demand, thereby reducing the possibility of the formation of all disinfection byproducts.

Neither chlorine dioxide, nor ozone, nor chloramines produce trihalomethanes at significant concentrations when used alone as disinfectants. Furthermore, the cost of any of these unit processes is very low. The major disadvantage of using alternate disinfectants for trihalomethane control relates to the lack of any precursor removal. Although no trihalomethanes will be produced as disinfection byproducts, other byproducts will still be produced as the oxidants (disinfectants) react with organic matter in the water. Further, some of these byproducts will be halogenated if chlorine dioxide or chloramines are used as the disinfectant alternative. Additionally, each of the disinfectants itself has inherent disadvantages; for example, ozone does not produce a residual for the distribution system; chloramine is a weaker disinfectant than free chlorine and may itself have unique toxicologic properties, and chlorine dioxide produces chlorite and chlorate as inorganic byproducts, anionic species whose health effect is currently unknown.

Each of these approaches has advantages and disadvantages as well as different degrees of effectiveness and unit costs, and these are detailed herein to help water utility managers, consulting engineers, Primacy Agencies, and others to choose the best approach to solve a given problem. Studies have shown that any of these techniques, if used properly and if final disinfection is applied diligently and monitored closely, can be used for trihalomethane control without any deterioration in bacteriologic quality at the consumer's tap.

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SECTION I
INTRODUCTION

Since the 1974 discovery of trihalomethane formation in drinking water as a result of chlorination,[1,2]* much research has been conducted to determine:

1. whether trihalomethanes affect the health of consumers;
2. how trihalomethanes should be measured;
3. how water quality conditions influence trihalomethane formation;
4. treatment technique(s) a drinking water utility could use to reduce trihalomethane concentrations in distributed water;
5. what effect altering treatment procedures to control trihalomethanes will have on the bacteriologic quality of distributed water; and
6. the cost of the various treatment possibilities.

The results of these studies were the basis for the U.S. Environmental Protection Agency's (USEPA) amendment to the National Interim Primary Drinking Water Regulations issued November 29, 1979—an amendment establishing a maximum contaminant level (MCL) of 0.10 mg/L total trihalomethanes (TTHM) in drinking water.[3]

Section 1401 (1)(D) of the Safe Drinking Water Act, Public Law 93-523, states that "the term 'primary drinking water regulation' means a regulation which contains criteria and procedures to assure a supply of drinking water which dependably complies with such maximum contaminant levels. . ." and Section 1412 (a)(2) states that "National interim primary drinking water regulations promulgated under paragraph (a)(1) shall protect health to the extent feasible, using technology, treatment techniques, and other means, which the Administrator determines are generally available (taking costs into consideration). . ." Thus, for any regulated contaminant, a "Treatment Techniques" document must accompany the establishment of a "Maximum Contaminant Level" (MCL) to provide compliance guidance. This research report† satisfies the treatment document requirement for the Trihalomethane Regulation and is a companion to the "Manual of Treatment Techniques for Meeting the Interim Primary Drinking Water Regulations," EPA-600/8-77-005 (April, 1978).[4] For further information on the Regulation,[3] the reader is referred to a document entitled "Trihalomethane Implementation Guidance"[5] that is available from the Office of Drinking Water, USEPA, Washington, D.C.

The purpose of this research report is to review the discovery of the problem; to summarize the results of research areas 1, 2, 3, 5, and 6 (above) and the Trihalomethane Regulation[3]; and to detail the results of the treatment studies, i.e., research area 4 (above).

The first five Sections of this report provide background information needed to understand and interpret the treatment research presented in Sections VI through VIII. In Section IX are summarized the findings concerning the impact of changing treatment to control trihalomethane concentrations on the bacteriologic quality in distributed water. This information will aid in understanding the interrelationship between disinfection practices, trihalomethane concentrations, and resulting bacteriologic quality. Section X on "Costs" will help the reader choose the most cost-effective treatment technique by combining the information in Sections VI through VIII on treatment effectiveness with the cost data in Section X. Section XI is a summary of treatment approaches with discussions of cost/effectiveness tradeoffs and examples of hypothetical situations that demonstrate how to select cost-effective treatment strategies for THM control.

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*Key papers are cited as references; the reader is referred to the literature citations in each of these papers for a more complete reading list.

†This work has been synopsized in "Removing Trihalomethanes from Drinking Water—An Overview of Treatment Techniques," J.M. Symons, A.A. Stevens, R.M. Clark, E.E. Geldreich, O.T. Love, Jr., and J. DeMarco. Water Engrg. & Mgmt., 128 (7): 50-53, 56, 61-64, July 1981.

Discovery

Although sporadic reports of the presence of chloroform and other trihalomethanes in finished drinking water occurred before 1974,[6] the reports that year by Rook[1] in The Netherlands and by Bellar, Lichtenberg, and Kroner[2] of USEPA clearly demonstrated that these contaminants were formed during the water treatment process as a result of chlorination. This finding prompted a survey in early 1975 of 80 water utilities in the United States, 79 of which practiced free residual chlorination or combined residual chlorination. This survey, the National Organics Reconnaissance Survey (NORS), showed that all of the water utilities that used free chlorine (sometimes called chlorine) in their treatment practice had varying concentrations of at least four trihalomethanes in their finished drinking water and that they were formed during treatment.[7] Follow-up studies[8] in 1975 and 1976, including the National Organics Monitoring Survey (NOMS), unpublished at this writing, confirmed this finding with samples collected at 113 locations during three different seasons.

These surveys, combined with like results from all over the world, showed that the reaction of chlorine to produce trihalomethanes was widespread and surely had been occurring for as long as chlorine had been in use in water treatment. Trihalomethanes in drinking water had usually escaped detection until 1974 because, before that time, the analytic techniques used to measure the organic content of water did not detect them. Once discovered, however, extensive research was begun to determine if their presence in drinking water was a health hazard for consumers. The results of the health effects studies that led up to the promulgation of the Trihalomethane Regulation[3] are summarized below.

Health Effects

People are exposed to chloroform in the air they breathe and the food they eat. Analysis of the relative contribution of chloroform in drinking water, air, and food assumes various levels of exposure based on monitoring studies. Drinking water may contribute from zero to more than 90 percent of the total daily body intake.

Chloroform has been shown to be rapidly absorbed on oral and intraperitoneal administration and to be subsequently metabolized to carbon dioxide, chloride ion, phosgene, and other unidentified metabolites. The metabolic profile of chloroform in animal species such as mice, rats, and monkeys is qualitatively similar to that in humans.

Mammalian responses to chloroform exposure include: central nervous system depression, hepatoxicity, nephrotoxicity, teratogenicity, and carcinogenicity. These responses are discernible in mammals after oral and inhalation exposures to high levels of chloroform ranging from 30 to 350 mg/kg of body weight, the intensity of response being dependent upon the dose. Although less toxicologic information is available for the bromine-containing trihalomethanes, mutagenicity and carcinogenicity have been detected in some test systems. Physiological activity is thought to be greater for the bromine-containing trihalomethanes than for chloroform.

Although short-term toxic responses to trihalomethanes in drinking water are not documented, the potential effects of chronic exposures to trihalomethanes should be a matter of concern. Prolonged administration of chloroform at relatively high dose levels, 100 to 133 mg/kg, to rats and mice manifested oncogenic effects. Oncogenic effects were not observed at the lowest dose levels, 17 mg/kg, in three experiments. Because methods do not now exist to establish a "threshold no effect" level of exposure to carcinogens, the preceding data do not imply that a "safe" level of exposure can be established for humans.

Human epidemiologic evidence is inconclusive, although several studies have found positive associations with some cancer sites. Eighteen retrospective studies, discussed in detail in Attachment 7 of the Trihalomethane Regulation,[3] have investigated some aspect of a relationship between cancer mortality or morbidity and drinking water variables. Because of various limitations in the epidemiologic methods, difficulties with the water quality data, and problems with the individual studies, the present evidence does not lead to a firm conclusion that an association exists between contaminants in drinking water and cancer mortality or morbidity; causal relationships cannot be proven on the basis of results from epidemiologic studies. When viewed collectively, however, the epidemiologic studies provide sufficient evidence for maintaining the hypothesis that a health risk may be occurring and that the positive relationships may be reflecting a causal association between constituents of drinking water and cancer mortality.

Using different models, the Science Advisory Board, the National Academy of Sciences, and USEPA's Carcinogen Assessment Group have estimated the incremental risks associated with the exposure from chloroform in drinking water. The exposure to chloroform from air and food has not been included in these computations. The risk estimates associated with the TTHM MCL of 0.10 mg/L are essentially the same from the National Academy of Sciences and the Carcinogen Assessment Group computations, i.e., they would predict an incremental risk of three to four per 10,000 population consuming 2 liters of water containing 0.10 mg/L chloroform daily for 70 years.

In summary, on the basis of the available toxicologic data, chloroform has been shown to be a carcinogen in mice and rats at high dose levels. Because its metabolic pattern in animals is qualitatively similar to that in humans, chloroform should be suspected of being a human carcinogen. Epidemiologic studies also suggest a human risk. Although documentation of other trihalomethane toxicity is not so well established, they should be suspected of posing similar risk. Because of these suspected health effects, the Trihalomethane Regulation was promulgated on November 29, 1979.[3] The Trihalomethane Regulation is summarized below.

Regulation

History—

Four statements in the *Federal Register*[3,9-11] trace the regulatory history of the control of organic contaminants in drinking water. The first statement was an Advance Notice for Proposed Rulemaking published July 14, 1976, in which the USEPA proposed several options for the control of trihalomethanes and other organic contaminants in drinking water and requested comments from the public.

As a result of this statement and the public comments, USEPA *proposed* a two-part Regulation for organic contaminant control in drinking water on February 9, 1978.[10] This document specified an MCL for the control of trihalomethanes and specified that a treatment technique, granular activated carbon, be installed at water utilities where source waters were significantly contaminated for the control of other synthetic organic contaminants.*

On July 6, 1978, the USEPA published supplemental technical information on this subject and extended the public comment period.[11] The final Regulation for the control of trihalomethanes only was published in the *Federal Register* on November

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*Note, although the February 9, 1978, *proposed* Trihalomethane Regulation[10] is often misunderstood to say that the USEPA was proposing to *require* the use of granular activated carbon adsorption for the control of trihalomethane concentrations, this was *not* the case.

29, 1979.[3] In this same document, the proposed regulation of other synthetic organic contaminants by using granular activated carbon treatment was deferred, and may be re-proposed at a later time.

On January 11, 1980, the American Water Works Association, together with the City of Englewood, Colorado, and the Capital City Water Company, a Missouri corporation, filed a Petition for Review with the U.S. Court of Appeals for the District of Columbia Circuit, asking the court for "a review of a final rule" as allowed by Section 1448 (a)(1) of the Safe Drinking Water Act (Public Law 93-523). At this writing no action has been taken on this Petition.

Summary of Trihalomethane Regulation (promulgated November 29, 1979)[3]—

Maximum Contaminant Level (MCL):

0.10 mg/L total trihalomethanes (TTHM) (Sum of concentrations of compounds 1, 2, 3, and 4, Table 1).

Applicability:

Community water systems that add disinfectant to the treatment process (ground and surface).

Effective:

Systems >75,000:	2 years after promulgation
Systems 10–75,000:	4 years after promulgation
Systems < 10,000:	Discretion of Primacy Agency (State, or USEPA if the State does not have primacy)

Monitoring Requirements:

Twelve-month-running average of a minimum of 4 samples per quarter per treatment plant taken on the same day. Systems using multiple wells drawing raw water from a single aquifer may, with Primacy Agency approval, be considered to have one treatment plant for determining the required number of samples.

Effective:

Systems > 75,000:	1 year after promulgation
Systems 10–75,000:	3 years after promulgation
Systems < 10,000:	Primacy Agency discretion

Sample Locations:

25 percent at extremity of the distribution system; 75 percent at locations representative of the population distribution.

Adjustment of Sampling Frequency:

For groundwater systems, reduced monitoring may be appropriate for certain systems. The Primacy Agency may reduce the requirements through consideration of appropriate data including demonstration by the system that the *maximum total trihalomethane potential** (MTP) is less than 0.10 mg/L. The minimum frequency would be one sample per year *for MTP* taken at the extremity of the distribution system. For groundwater systems not meeting the above MTP limit and for surface water systems, the Primacy Agency may reduce the monitoring requirements if, after 1 year of data collection, TTHM concentrations are consistently below 0.10 mg/L. The minimum frequency would be one sample per quarter per treatment plant *for total trihalomethanes* taken at the extremity of the distribution system. The original frequency would be reinstated if the TTHM concentrations exceed 0.10 mg/L or if the treatment or source is modified.

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*The maximum total trihalomethane potential is defined as the total trihalomethane concentration in a sample after storage for 7 days at 25°C (77°F) or above in the presence of a *disinfectant* residual or after the use of USEPA method 501.1 if no *disinfectant* residual is present after initial storage.

Reporting Requirements:

To Primacy State:

Average of each quarterly analysis, within 30 days. Until Primacy States have adopted the regulations, reporting will be to USEPA unless Primacy State requests receipt of data.

To Public and Primacy State:

Running-12-month average of each quarterly sample if total trihalomethane concentration exceeds MCL, as prescribed by the public notification provisions.

Other Requirements:

To Ensure Microbiologic Quality:

Primacy Agency approval of *significant* modifications in the treatment process for the purpose of meeting the TTHM MCL.

Analytic Requirements:

In accordance with specified methods (purge and trap or liquid-liquid extraction) conducted by certified laboratories (see Section II, Measurement).

As a further aid to understanding the Regulation[3] the reader is referred to the document "Trihalomethane Implementation Guidance"[5] that is available from Office of Drinking Water, USEPA, Washington, D.C. The Appendix contains the entire Trihalomethane Regulation from the *Federal Register*.

SECTION II
MEASUREMENT

Appendix C of the Trihalomethane Regulation[3] contains a detailed description of the USEPA approved methods for sampling and analyzing drinking water for trihalomethane concentrations. These techniques are summarized here so that the reader will understand the general approach.

Sample of Collection and Handling

1. The sample containers should have a total volume of at least 25 mL. Narrow-mouth screw cap bottles with polytetrafluoroethylene (PTFE) faced silicon septa cap liners are strongly recommended.
2. If the trihalomethane concentration at the time of sampling is desired, a chemical reducing agent, sodium thiosulfate or sodium sulfite, must be added to the sample to arrest the formation of trihalomethanes after sample collection. If chemical stabilization is employed, the reagent must be also added to the blanks.
3. The sample bottles are filled in such a manner that no air bubbles pass through the sample as the bottle is filled. The sample is then inverted; the absence of entrapped air indicates a successful seal.
4. If a chemical reducing agent has been added to the sample bottle, the bottle is shaken vigorously for 1 minute after sealing the bottle.
5. Blanks are prepared in duplicate at the laboratory by filling and sealing sample bottles with waters containing a low concentration of organics just before shipping the sample bottles to the sampling site. The blanks are shipped to and from the sampling site along with the sample bottles. The blanks and the samples collected at a given site are stored together.
6. The procedure recommends that all samples be analyzed within 14 days of collection.

Measurement Techniques

Although other techniques were investigated,[12] the USEPA has approved two gas chromatographic (GC) techniques for the measurement of trihalomethanes. These are generally called the "Purge and Trap" and "Liquid-Liquid Extraction" techniques. Although both methods have advantages and disadvantages, when performed properly, they have been shown to produce equivalent results for trihalomethane analysis.[13] The two appoved methods are summarized below:

Purge and Trap Summary—

1. Trihalomethanes are purged by an inert gas that is bubbled through the aqueous sample. The trihalomethanes, along with other organic constituents that exhibit low water solubility and a vapor pressure significantly greater than water, are efficiently transferred from the aqueous phase to the gaseous phase. These compounds are swept from the purging device and are trapped in a short column containing a suitable sorbent. After a predetermined time, the trapped components are thermally desorbed and backflushed onto a gas chromatographic column and separated under temperature programmed conditions. Measurement is accomplished with a halide specific detector such as electrolytic conductivity or microcoulometric titration.

2. Confirmations of identity may be obtained using dissimilar columns, or by mass spectrometry (MS).

3. Aqueous standards, blanks, and unknowns are purged and analyzed under identical conditions to compensate for varying purging recoveries.

4. The total analysis time, assuming the absence of other organohalides, is approximately 35 minutes per sample.

Liquid-Liquid Extraction Summary—

1. Ten mL of sample are extracted at one time with 2 mL of solvent (pentane, hexane, or methylcyclohexane). Three μL of the extract are then injected into a gas chromatograph equipped with a linearized electron capture detector for separation and analysis. The absence of trihalomethane peaks in the raw water is generally ample evidence of an interference-free finished water analysis.

2. When needed, confirmatory evidence may be obtained using dissimilar columns and temperature programming. When component concentrations are sufficiently high (>50 μg/L), halide specific detectors may be employed for improved specificity. Unequivocal confirmations of identity at high concentrations (>50 μg/L) can be obtained using MS in place of the electron capture detector. At concentrations below 50 μg/L, unequivocal confirmation of identifications can only be performed by the purge and trap technique outlined above.

3. Standards are dosed into water with a low concentration of organics, and the standards are extracted and analyzed in a manner identical to the samples to compensate for possible extraction losses.

4. The extraction and analysis time is 10 to 50 minutes per sample depending upon the chromatographic conditions chosen.

Units of Concentration—

Because the gas chromatographic techniques used to measure trihalomethanes are based on gravimetric (weighed) standards, and because the Trihalomethane Regulation[3] is based on total trihalomethanes summed on a weight basis, μg/L, trihalomethane concentrations are most often seen in the literature expressed in this manner. Frequently, however, expressing the concentration in terms of chemical equivalents (micromoles/L) is more desirable. Chemical equivalents are an expression of the number of *molecules* present ($6.02 \times 10^{17}/\mu$mol), and are, therefore, a better unit of expression when concentrations of reactive sites (precursors) or active sites (adsorption) are being discussed because the interpretation of research results will not be influenced by the differing molecular weights of the trihalomethanes present in various mixtures. Throughout this document, both systems of units are used. In detailed *interpretation* of research results, the units of μmol/L are the most appropriate; however, to aid the reader in judging the success of a water utility to meet the Trihalomethane Regulation,[3] the data are more often reported in terms of *weight* concentration (μg/L) rather than, or in addition to, the more chemically meaningful *molecular* concentration (μmol/L).

Quality Assurance

The USEPA has set a requirement that, to be approved, a laboratory must be able to measure the concentration of the individual trihalomethanes as well as the TTHM concentration in a quality control sample supplied by USEPA to within ±20 percent of the "true" value. This determination must be made annually. If, after an investigation of its procedures, a laboratory cannot meet this requirement, it is allowed to demonstrate its effectiveness on repeat quality control samples.

Surrogate Measurements

Because the analysis for the presence of trihalomethanes is a GC procedure requiring skilled operators and some time to complete, a simple rapid surrogate measurement that would predict trihalomethane concentrations seemed desirable. Because chlorine reacts with precursors to form trihalomethanes, a test that would measure the precursor concentrations in water was thought to be useful for predicting trihalomethane concentrations.

No direct test for trihalomethane precursors exists,* so a test for general organic content was considered as an alternative. The difficulty with using a general organics test as a measure of trihalomethane precursors is that precursor concentrations are not a constant percentage of the general organic content. Nevertheless, in the report of the National Organics Reconnaissance Survey,[7] nonpurgeable organic carbon† (NPOC) was proposed as a surrogate analytic test for the trihalomethane measurement. The report[7] suggested that raw water NPOC concentrations could be used to predict TTHM concentrations in micromoles per liter in finished water (1 μmol/L is approximately 120 μg/L as $CHCl_3$).

For the analysis of the data in Reference 7, the NPOC data were grouped in concentration ranges and the mean TTHM concentration for all data in a given NPOC range was plotted against the mid-point of the given NPOC range. These data were very linear when plotted arithmetically. Subsequent research (see Section III, Mechanism of Formation) showed, however, that several water quality conditions such as precursor type, temperature, pH, bromide concentration, and disinfectant type, as well as time of exposure to free chlorine before measurement influenced the resulting TTHM concentration in a given location. Therefore, the suggestion noted above was reviewed.

Figure 1, in which all the data from the NORS[7] are plotted, shows the scatter around the line of best fit by least squares. The correlation coefficient, 0.77, is highly statistically significant, showing that, in general, waters with higher NPOC concentrations will produce more trihalomethanes than waters with lower NPOC concentrations. The scatter, however, is great, as demonstrated by the high calculated 95 percent confidence limit, ±0.5 μmol TTHM per liter (approximately ±60 μg/L as $CHCl_3$) around the mean.

The unpublished data from the National Organics Monitoring Survey confirmed this lack of precise prediction, although there, finished water NPOC concentrations were correlated with finished water TTHM concentrations. Similar findings resulted from a USEPA-sponsored project at the Jefferson Parish, Louisiana, water treatment plant.[14]

Therefore, reasonably *precise* predictions of trihalomethane concentrations *cannot* be made from NPOC measurements because of variations in yield caused by the environmental factors noted above and discussed in Section III, below. This concept was missing from Reference 7, and therefore, the conclusion relating to the relationship between NPOC and trihalomethane concentrations was overstated therein. The only demonstrated reliable method of precisely determining the trihalomethane concentration is to obtain the necessary equipment and technical staff to perform the analysis directly.[3] Only with considerable experience of comparative results between direct TTHM measurements and NPOC determinations may a given utility be able to effectively use the simpler NPOC measurement as a useful surrogate parameter.

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*A method for measuring trihalomethane precursors indirectly is discussed in Section IV, Measurement for Treatment Evaluation.

†That portion of the total organic carbon concentration that remains in a sample after the carbon dioxide has been purged under acid conditions.

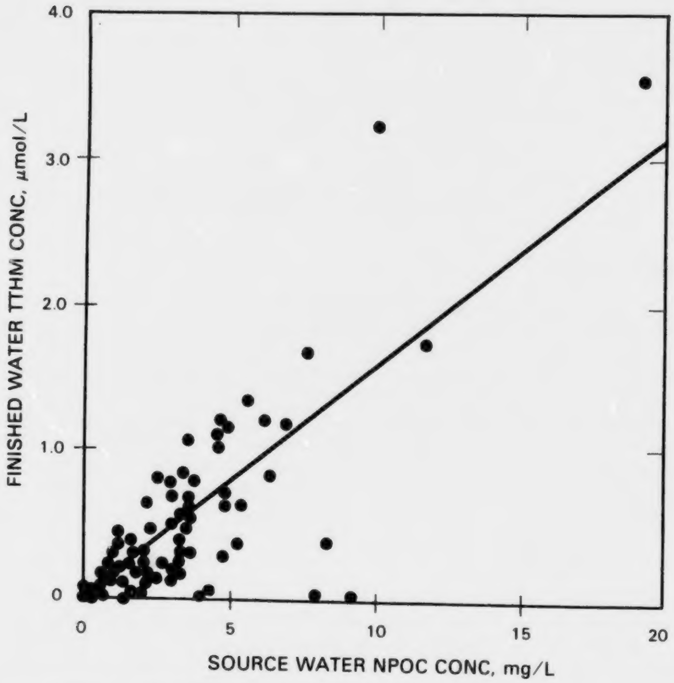


Figure 1. Raw water nonpurgeable organic carbon vs. finished water total trihalomethanes. (Data obtained from the National Organics Reconnaissance Survey.[7])

SECTION III
MECHANISM OF FORMATION

Nomenclature

For those readers unfamiliar with organic nomenclature, the following discussion defines some of the terms. Although methane gas does not seem to be involved, the reaction of chlorine in water with certain organic compounds, under certain conditions, produces a group of halogen-substituted single carbon compounds. These compounds are *named* as derivatives of methane (CH_4) (Table 1).

Under typical circumstances, the trihalomethanes produced in drinking water are dominated by compounds 1 and 2, but compounds 3 and 4 are frequently found and compounds 5 and 6 have been detected (Table 1). Note, the arithmetic sum of the concentrations of compounds 1, 2, 3, and 4 has been defined in the Trihalomethane Regulation[3] as "Total Trihalomethanes" (TTHM).

General Mechanism

The formation of trihalomethanes during free chlorination of drinking water results from a complicated mechanism of attack by aqueous halogen species on natural aquatic humic substances, i.e., humic and fulvic acids, rather than organic compounds whose source is industrial water pollution. Thus, trihalomethanes result from the generalized reaction:

FREE CHLORINE + PRECURSORS (HUMIC SUBSTANCES) AND BROMIDE → TRIHALOMETHANES + OTHER BYPRODUCTS

Several factors influencing this reaction[15-17] are summarized below. Design of the most effective treatment strategy depends on a knowledge of the trihalomethane formation reaction and the factors controlling it.

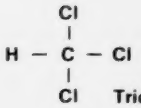
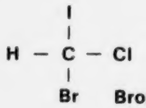
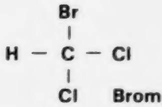
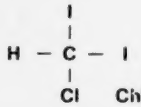
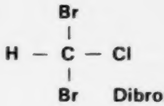
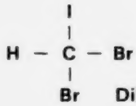
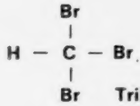
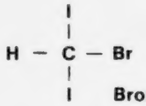
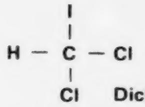
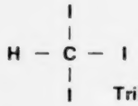
Effect of Time

The formation of trihalomethanes under natural conditions is not instantaneous. Although, under some reaction conditions the formation of trihalomethanes may be completed in less than an hour, in other circumstances, several days may be required before the maximum yield of trihalomethanes occurs.

Varying apparent "yields" of trihalomethanes reported throughout the literature under varying reaction conditions may be influenced by the reaction rate. Thus, a lower reported "yield" may be the result of the reaction proceeding toward "completion" at a slower rate. Reaction conditions may also, however, influence the yield of trihalomethanes obtained at a time when no further reaction appears to be occurring.

The precise effect on the kinetics (rate) of trihalomethane formation of various parameters influencing it or yield at "completion" of the reaction is difficult to predict because of the complexity of the reactions between aqueous free chlorine and the mixture of precursors of largely unknown structure. Thus, from a practical standpoint, when yield of trihalomethanes is discussed, the time allowed for the reaction and other conditions discussed below must be defined.

TABLE 1. STRUCTURAL FORMULAS AND NAMES OF THE TRIHALOMETHANES

Formula	Name	Formula	Name
1.  $\mathrm{H-\overset{Cl}{\underset{Cl}{C}}-Cl}$	Trichloromethane (Chloroform) $CHCl_3$	6.  $\mathrm{H-\overset{I}{\underset{Br}{C}}-Cl}$	Bromochloroiodomethane $CHClBrI$
2.  $\mathrm{H-\overset{Br}{\underset{Cl}{C}}-Cl}$	Bromodichloromethane $CHBrCl_2$	7.  $\mathrm{H-\overset{I}{\underset{Cl}{C}}-I}$	Chlorodiiodomethane $CHClI_2$
3.  $\mathrm{H-\overset{Br}{\underset{Br}{C}}-Cl}$	Dibromochloromethane $CHBr_2Cl$	8.  $\mathrm{H-\overset{I}{\underset{Br}{C}}-Br}$	Dibromoiodomethane $CHBr_2I$
4.  $\mathrm{H-\overset{Br}{\underset{Br}{C}}-Br}$	Tribromomethane (Bromoform) $CHBr_3$	9.  $\mathrm{H-\overset{I}{\underset{I}{C}}-Br}$	Bromodiiodomethane $CHBrI_2$
5.  $\mathrm{H-\overset{I}{\underset{Cl}{C}}-Cl}$	Dichloroiodomethane $CHCl_2I$	10.  $\mathrm{H-\overset{I}{\underset{I}{C}}-I}$	Triiodomethane (Iodoform) CHI_3

Effect of Temperature

When Ohio River water was chlorinated in the laboratory, increasing the temperature had a positive effect on trihalomethane formation[15] (Figure 2). A corresponding seasonal variation, noticed at a water utility using the same source, has been shown to be largely a temperature effect. Thus, trihalomethane control problems become more acute during hot weather when water temperatures are higher during treatment and distribution.

Data collected by the Ohio River Valley Water Sanitation Commission (ORSANCO)[18] showed that at several water utilities the finished water TTHM concentrations varied seasonally and were lower in the winter when water temperatures were lower, although data were not controlled for possible variations in precursors and other treatment condition variables (Figure 3).

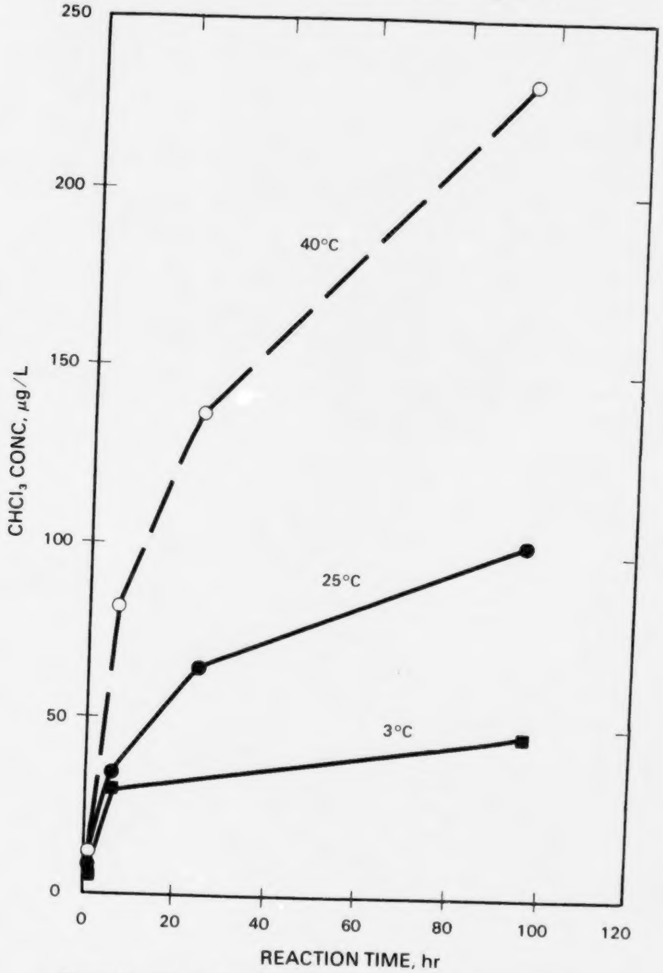


Figure 2. Effect of temperature on chloroform formation.[15]

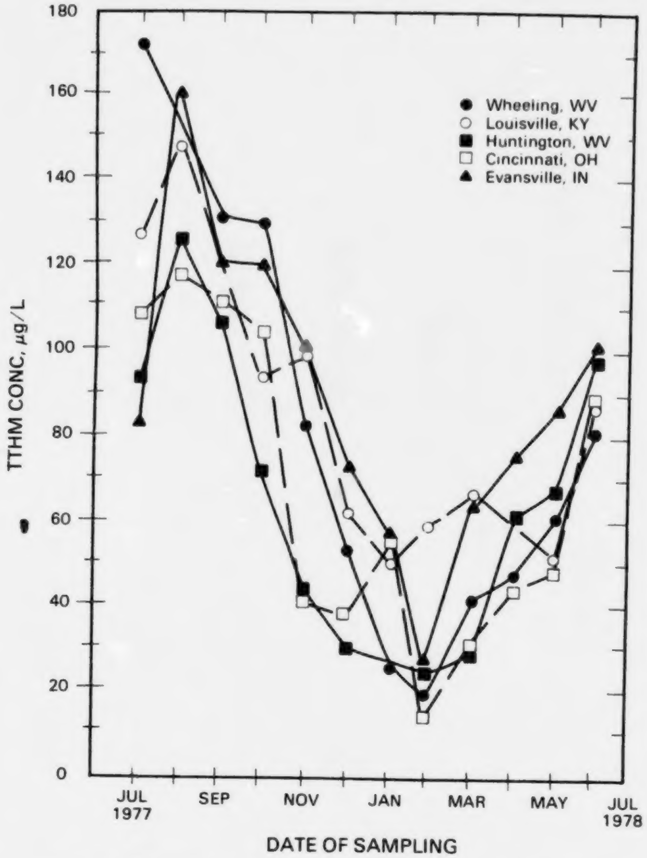


Figure 3. Seasonal variation in finished water TTHM concentration for treated surface waters.[18]

Effect of Bromide and Iodide Concentration

Bromide and iodide ions are oxidized by aqueous chlorine to species capable of participating in organic substitution reactions resulting in the formation of pure- and mixed-halogen trihalomethanes. When Bunn et al.[19] chlorinated Missouri River water in the presence of added fluoride, bromide, and iodide, they first confirmed one of Rook's suspicions that this could occur in aqueous systems. They observed the formation of all ten possible chlorine-, bromine- and iodine-containing pure- and mixed-halogen trihalomethanes shown in Table 1. On a theoretical basis, oxidation of fluoride by aqueous chlorine to active fluorine species followed by substitution was not expected and was not observed.

Figures 4A and 4B illustrate the effect that adding bromide has on the ratio of trihalomethanes produced during the reaction of aqueous chlorine with humic acids. Note that bromine substitution is favored over chlorine, even though chlorine is present in large excess compared with the initial bromide.

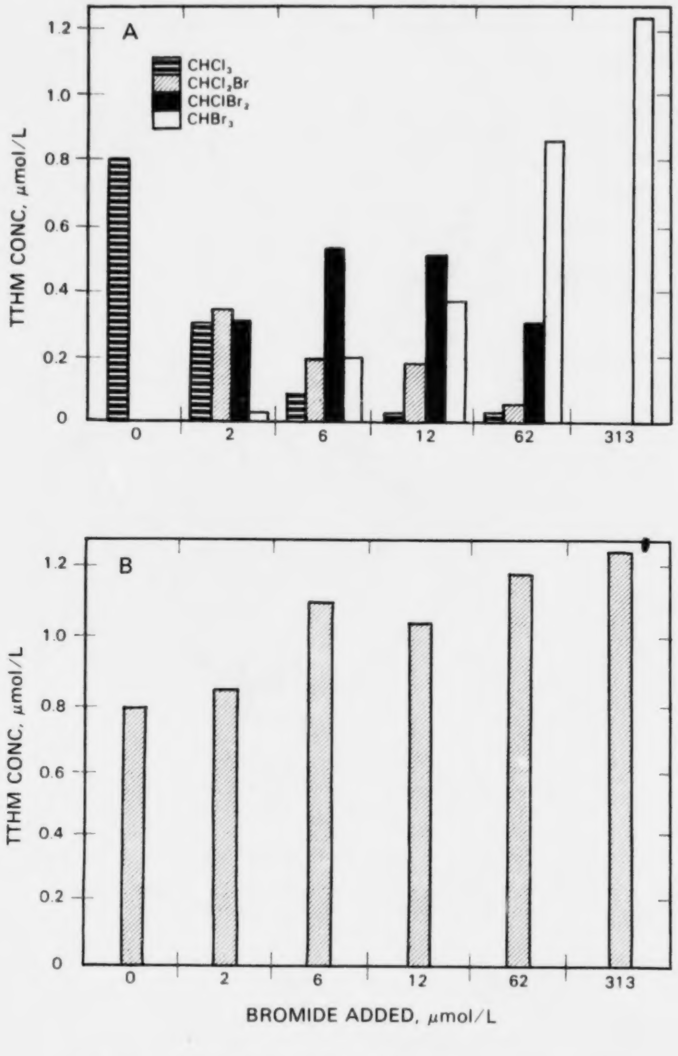


Figure 4. Trihalomethanes formed by reaction of humic acid with aqueous chlorine in the presence of varying bromide ion concentrations using a chlorine dose of 282 microequivalents per liter.

For example, in the experiment where 12 μmol bromide/L were added to the solution containing the humic acid and 282 μequivalents chlorine/L, the oxidant ratio, Cl_2/Br_2 was 23, but the reacted Cl/Br ratio in the trihalomethanes formed was only 0.42 (Figure 4A). Thus, bromine competes more effectively than chlorine for active sites on the humic acid precursor molecule, perhaps mechanistically by way of a faster substitution reaction rate. A probable example of this effect occurred in a coastal city, Brownsville, TX, that had a finished water with the following concentrations of trihalomethanes: chloroform, 12 μg/L; bromodichloromethane, 37 μg/L; dibromochloromethane, 100 μg/L; and bromoform, 92 μg/L.[7]

Additionally, the total molar yield of trihalomethanes appears to increase with increasing bromine substitution. Without any added bromide, 0.8 μmol TTHM/L was formed, but when 313 μmol of bromide/L was added to the solution, the TTHM yield was 1.25 μmol/L, Figure 4B. This was also observed when pure aqueous bromide was reacted with the humic acid under the same conditions as aqueous chlorine. Reactions in these experiments were allowed to proceed over a period of many days until detectable changes in trihalomethane concentrations were small. Nevertheless, the apparent higher "yields" obtained with bromination may be only a kinetic effect of faster formation of brominated species. This interpretation is supported by a qualitative observation that the favored bromine-containing species formation was more pronounced in the early stages of reaction. Although few utilities may experience this kind of problem, either cause of high trihalomethane concentrations will create a larger TTHM problem for utilities that experience the presence of bromide. For example, increases in TTHM concentrations during the time of treatment have been reported at a water treatment plant in Contra Costa, CA, where sea water intrusion was temporarily responsible for increases in bromide (Figure 5).[20]

Effect of pH

Numerous workers have shown that increasing the pH of the water being treated dramatically influences rates of formation of trihalomethanes during water treatment. Figure 6 presents one example. Given sufficient time, however, the yields for the two pH systems may be similar. Note that the two lines in Figure 6 are still approaching each other after 70 hours. The increase of trihalomethane formation rate with pH was expected, because the classic haloform reaction is base catalyzed; however, this explanation is likely to be an oversimplification where rather complex humic acid structures are involved. Simple methyl ketones, models for the haloform reaction, have been shown to react too slowly to account for trihalomethane formation under most drinking water treatment conditions.

Figure 7 shows the results of attempts to react chlorine at pH 7 with simple acetyl compounds (acetone, acetaldehyde, and acetophenone) when these compounds were spiked at 5 μmol/L into raw and granular activated carbon (GAC) treated water. Under these circumstances, trihalomethanes were not produced at rates significantly higher than those for the blank samples. Figure 8, however, shows that at higher pH values, the simplest methyl ketone, acetone, reacts at a much higher rate, and this class of compounds could become a significant source of precursor in those pH ranges. The complex humic structure, therefore, must have more active groups than the simple methyl ketones for chlorine substitution to account for reactivity at pH 7, with the possibility of less active acetyl groups becoming more significant at higher pH, increasing reaction rate and possibly yield.

An alternative explanation for the effect of pH on rate and yield with humic acid precursor has been suggested by Christman, however (R.F. Christman, Univ. North Carolina, Chapel Hill, 1977, personal communication). The macromolecule may simply be "opening up" by mutual repulsion of the negative charges at high pH, thus increasing the availability of additional reactive sites on the molecule.

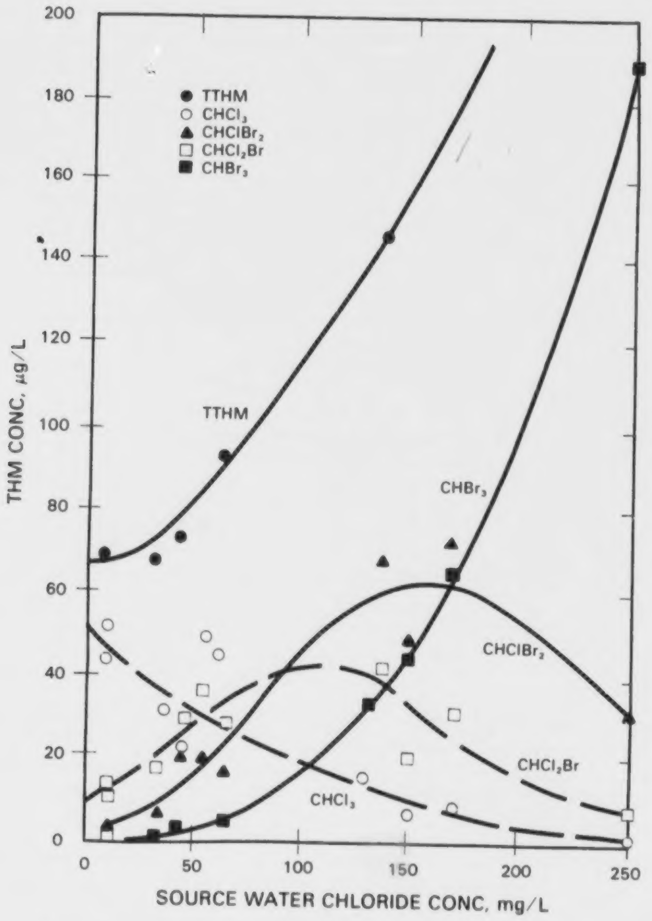


Figure 5. Effect of salt water intrusion on THM formation potential.[20] (Adapted from JOURNAL American Water Works Association, Volume 70, No. 11 [November 1978] by permission. Copyright 1978, the American Water Works Association.)

Effect of Characteristics and Concentration of Precursors

Increasing the concentration of humic acid precursor in the presence of excess chlorine with otherwise constant reaction conditions caused trihalomethane yields to increase in direct proportion to the humic acid dose (Figure 9). At similar NPOC concentrations, humic acids and natural water have been shown to result in similar trihalomethane yields (Figure 10, page 19). When different source waters are compared, however (see Section II, Surrogate Measurements) only crude relationships have been found between organic carbon concentrations and trihalomethane yields.

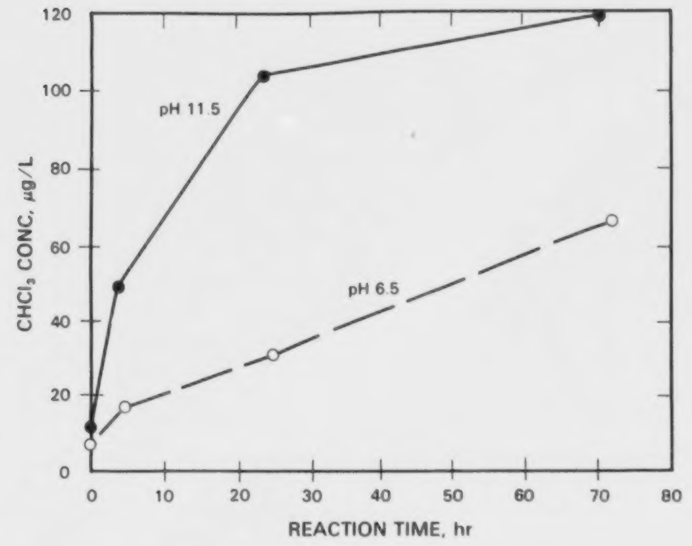


Figure 6. Effect of pH on chloroform production, settled water, 25°C (77°F), 10 mg/L chlorine dose.[15]

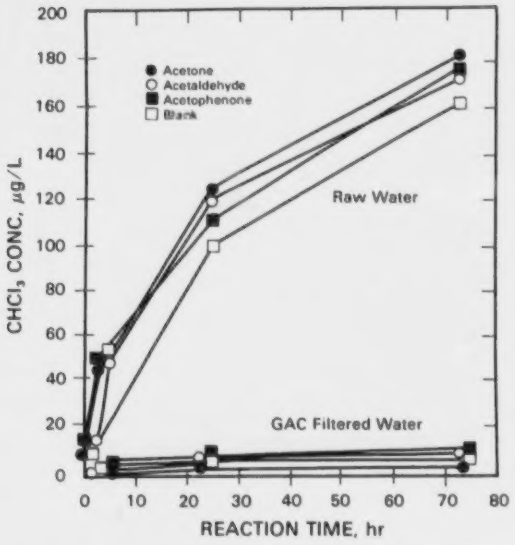


Figure 7. Raw and GAC filtered water spiked at 5 µmol/L with low molecular weight acetyl compounds. pH 7.0; 10 mg/L chlorine dose.[15]

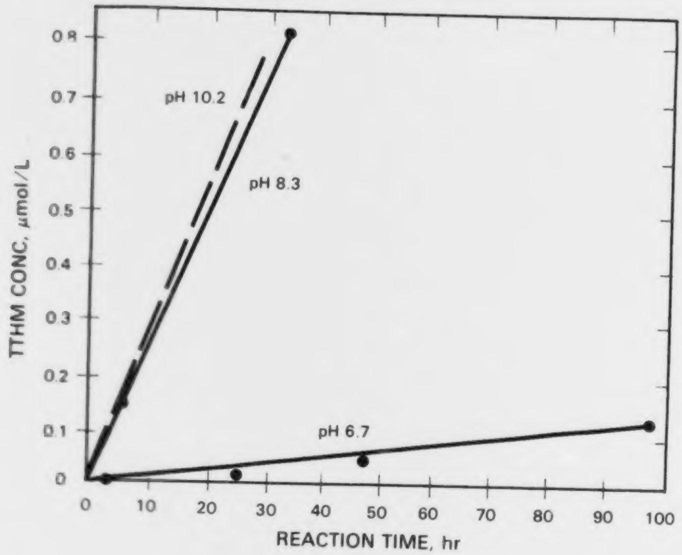


Figure 8. Effect of pH on trihalomethane production from acetone. 1 mg/L; 25°C (77°F); 10 mg/L chlorine dose.[15]

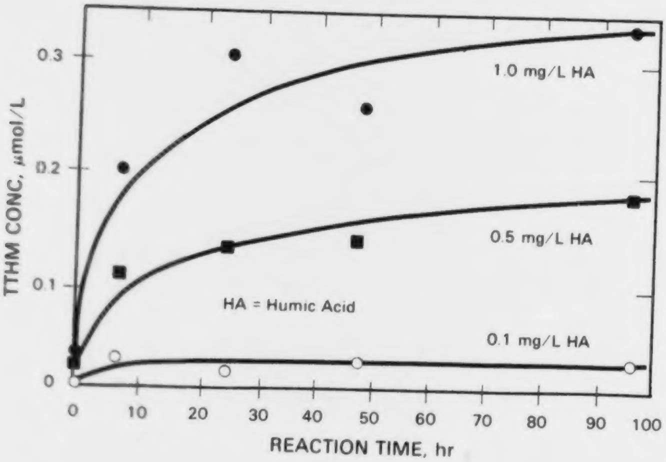


Figure 9. Effect of humic acid concentration on trihalomethane production. pH 6.7; 25°C (77°F); 10 mg/L chlorine dose.[15]

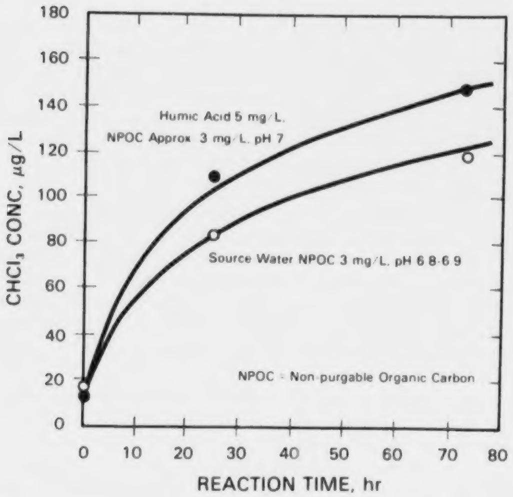


Figure 10. Comparison of humic acid, source water reaction rates at similar NPOC concentrations. 10 mg/L chlorine dose.[15]

Further, rate curves take on distinctly different shapes depending on the source of precursor substances. The work of Rook[21] shows the reaction of fulvic acid solutions to be characteristic of *m*-dihydroxyphenyl moieties, e.g., resorcinol, as that reaction is nearly complete at near neutral pH in less than 2 hours (Figure 11). Quite a different characteristic curve is observed with Ohio River water precursor and a different source of humic acid (Figure 10), however, where the reaction takes place relatively slowly over a period of many days.

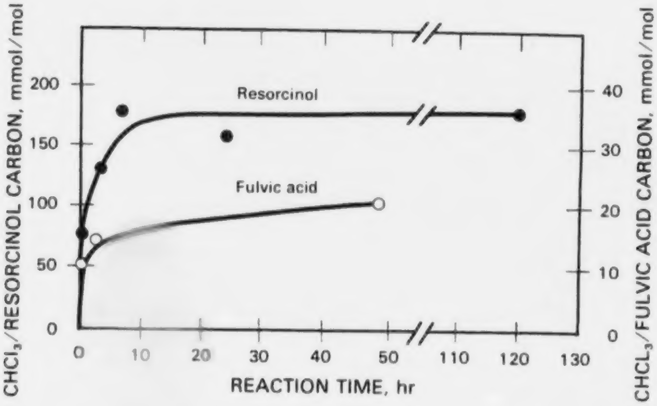


Figure 11. Reaction of model precursors with aqueous chlorine.[16]

The probable differences in precursors at different locations have been further demonstrated. As expected on a theoretical basis, treatment of resorcinol and *m*-dihydroxybenzoic acid solutions with potassium permanganate at low dosages was nearly 100 percent effective in preventing the formation of trihalomethanes upon chlorination of these substances, yet potassium permanganate was only marginally (10% to 20%) effective in reducing the ability of Ohio River precursors to form trihalomethanes upon subsequent chlorination. (This work is discussed more completely on pages 129 to 135.)

Research by Christman and his team[22] is attempting to understand the structure of aquatic humic and fulvic acids and their roles in the trihalomethane reaction. To date, scores of substructure moieties have been identified through the use of controlled oxidative and hydrolytic degradation procedures coupled with sophisticated GC/MS identification techniques. Representative models selected from these have been reacted with aqueous free chlorine to show that trihalomethanes, as well as other chlorinated byproducts, may be formed by a number of different pathways and at vastly different rates.

The above serves to indicate that although precursor materials from various water sources may be of largely natural origin, the composition of that material is likely to be different depending on the type of source water involved and the origin of precursors in the watershed. Considerably more work is needed, therefore, to understand precisely the complex mechanisms of trihalomethane formation during drinking water chlorination.

Effect of Chlorine Dose and Type

Where precursor is kept constant, only a slight influence on trihalomethane formation rate or yield occurs when the free chlorine dose is increased beyond the demand (Figure 12). Additionally, work by Kajino and Yagi (Figure 13) showed that once chlorine demand was satisfied, increasing chlorine residual concentrations had little influence on chloroform yield in the 8-hr reaction time.[23] Both similar[20,24,25] and contrary[26,27] results have been reported while conducting tests with different sources of precursor. Combined chlorine (chloramines) does not cause the formation of trihalomethanes (Figure 14).

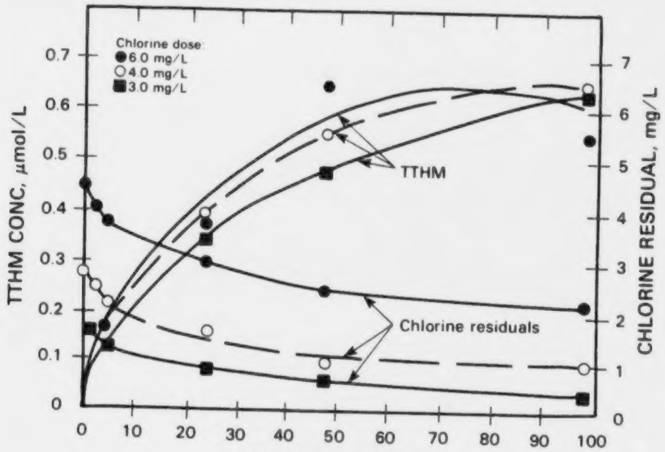


Figure 12. Effect of chlorine dose on trihalomethane formation. pH 7.0; 25°C (77°F).[16]

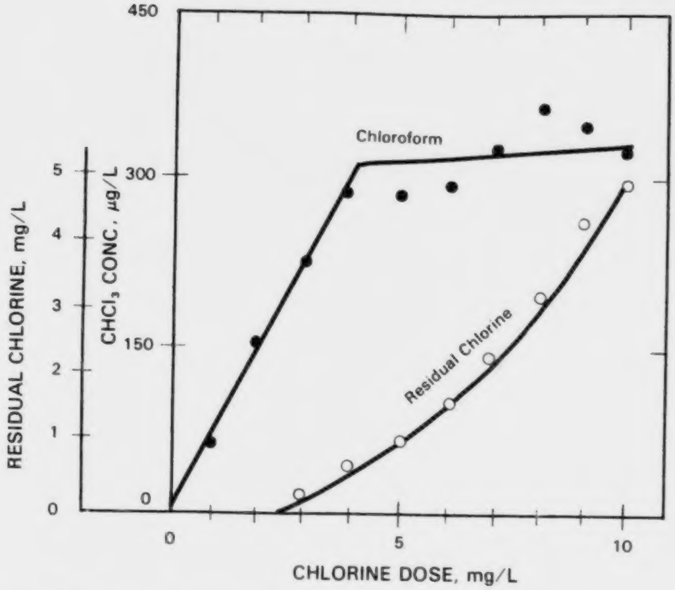


Figure 13. Chloroform formation compared with chlorine residual.[23]

Because of the possible significance of free chlorine concentration under some circumstances and the importance of precursor concentration discussed above, the manner in which the chlorine is added to the water (initial mixing and reactor design) is likely to impact the rate of formation of trihalomethanes and therefore their concentrations after treatment.

All of the factors discussed here influence the concentration of trihalomethanes each consumer in a given utility's distribution system will receive. As mentioned above, all must be understood if the success of a proposed treatment change at a given utility is to be properly evaluated. Section IV will show how these factors are applied during any treatment evaluation.

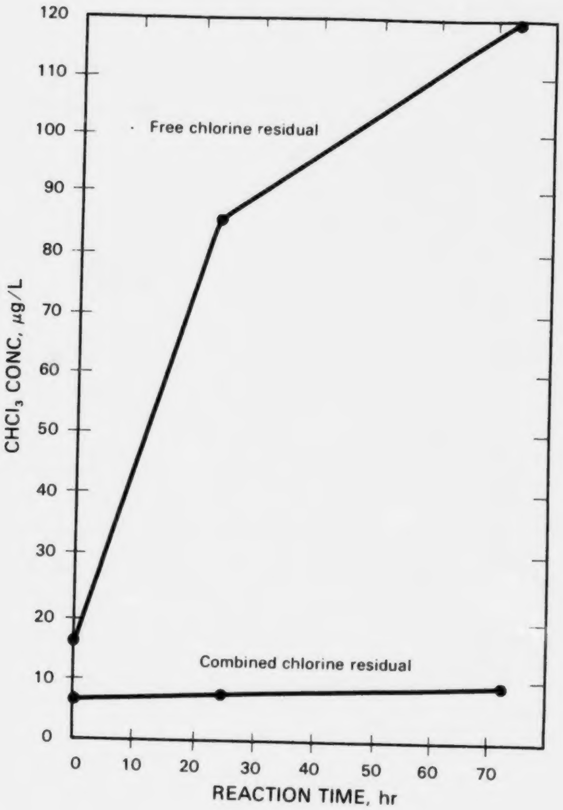


Figure 14. Chloroform formation by free and combined chlorine residual.[15]

SECTION IV
MEASUREMENT FOR TREATMENT EVALUATION

Definitions

To understand the measurements that must be made to evaluate treatment success, four definitions are important.

1. Instantaneous trihalomethane (InstTHM) concentration — The concentration of trihalomethanes in the water at the moment of sampling. This may be expressed in terms of the individual species or their sum as total trihalomethanes (TTHM). This is the parameter measured in the distribution system to provide the data needed to judge compliance with the Trihalomethane Regulation.[3]

2. Terminal trihalomethane (TermTHM) concentration* — The concentration of trihalomethanes that occurs at the termination of the measurement of this parameter. To measure TermTHM concentration, the chlorine-precursor reaction conditions are selected according to the treatment practiced at the particular water plant being evaluated. In general, a sample of water is chlorinated under these conditions, and chloroform and the other trihalomethane species are measured after a specified time period, as explained below.

TermTHM concentration is equally important as a parameter for evaluating consumer risk as is the InstTHM concentration. Because this parameter is a measure of the sum of the amounts of trihalomethanes already present (instantaneous) and those formed during the reaction time, a third parameter, useful for evaluating unit process performance for removal of unreacted precursor, must be defined (Definition 3, below).

3. Trihalomethane formation potential (THMFP) — Calculated as the *increase* in trihalomethane concentration that occurs during the storage period in the determination of the TermTHM concentration. The THMFP is obtained by subtracting the InstTHM concentration from the TermTHM concentration, either when total trihalomethanes or when the individual species data are used. THMFP is a measure of the *portion* of the *total* precursor material (see Definition 4 below) that is in the water at a given point in the treatment train and, therefore, is of most concern to the water utility operator. This parameter, when computed on unit process influent and effluent samples, can be used to determine the efficiency of the process being used to remove the pertinent fraction of precursor material.

4. Total precursor — The concentration of *all* trihalomethane precursor materials present in the water that *could* react with halogen species under conditions that maximize the yield of trihalomethanes. A distinction between THMFP and total precursor is important. No standardized procedure for measuring this parameter exists, however, and considerable research would be required to establish the optimum conditions to ensure the complete reaction of *all* precursors to yield the *theoretical maximum* trihalomethane concentrations.

Because the chlorination conditions for the TermTHM concentration measurement are somewhat less than optimum for trihalomethane formation, the

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*TermTHM is not to be confused with the Maximum Total Trihalomethane Potential (MTP) mentioned in the Trihalomethane Regulation[1] and in Section I, Summary of Regulation. They are different parameters. The goal of MTP is to define the upper limit of the possible total trihalomethane concentration in certain water utilities treating groundwater. MTP is not a quantitative index of trihalomethane precursor concentrations as is the TermTHM parameter. Also, TermTHM should not be confused with other proposed techniques designed to hasten the reaction between chlorine and precursor by heating and pH elevation or with "Total Potential Haloforms," measured by a direct aqueous sample injection technique,[28] that are likely to give unrealistic estimates of *pertinent* precursor concentrations.[12]

TermTHM concentration obtained in any test will be somewhat less than the *theoretical maximum* trihalomethane concentration. Thus, the value obtained for THMFP under these conditions will be smaller than the theoretical "total precursor" parameter. Although the value obtained, THMFP, is not the "total precursor" concentration, as noted above, it is an index of the concentration of materials of most concern relative to trihalomethane formation at a particular water treatment plant and in that distribution system. To compare treatment results from utility to utility nationwide or within a utility where reaction conditions caused by differing treatment conditions exist, selection of a single set of standard test conditions may seem desirable. This potential comparability, however, is less desirable than the direct evaluation of precursor removal within the utility under study where that utility is evaluating its own capabilities to meet the trihalomethane MCL. The TermTHM and THMFP test conditions are intentionally left flexible here to encourage the individual utility to select conditions for the test to reflect their individually most promising treatment options. Although this test approach makes inter-utility comparisons of treatments very difficult, the approach makes treatment evaluation measurements better predictors of eventual success at that utility. The option exists, of course, in any collection of research efforts to conduct the precursor test under any one or a multiple of several sets of conditions to allow for direct comparisons of precursor removal results within one or between any number of utilities conducting similar treatment experiments. Figure 15 graphically presents the parameters discussed.

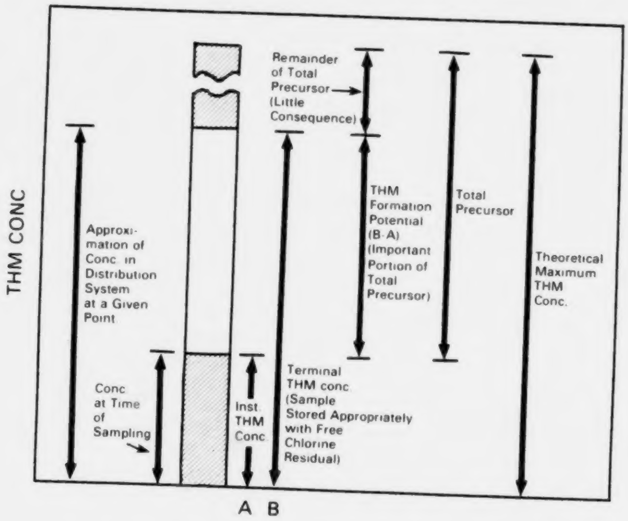
THM CONC
Remainder of Total Precursor (Little Consequence)
THM Formation Potential (B-A) (Important Portion of Total Precursor)
Total Precursor
Theoretical Maximum THM Conc.
Approximation of Conc in Distribution System at a Given Point
Conc at Time of Sampling
Inst THM Conc
Terminal THM conc (Sample Stored Appropriately with Free Chlorine Residual)
A
B

Figure 15. Trihalomethane measurement parameters.

Measurement of Instantaneous THM Concentrations

For an InstTHM concentration measurement, the reaction of chlorine with precursor materials must be halted at the time of sampling with the goal being to measure only trihalomethanes present at that time. A small amount of reducing agent, sodium sulfite or sodium thiosulfate, is added to the sample to react with the chlorine and, thus, render the chlorine unavailable for oxidation or substitution reactions. This technique is used in the samples required for compliance with the Trihalomethane Regulation.[3]

A small increase in trihalomethane concentrations upon storage after addition of the reducing agent usually is observed, even when the mixing of the reducing agent is nearly instantaneous. This is probably caused by a slow hydrolysis of certain trihalo-intermediates; the hydrolysis step does not require the presence of chlorine. The distinction should be made between this minor effect on the InstTHM concentration and the continued trihalomethane formation reaction when no reducing agent is added (discussed below). The increase in trihalomethane concentration during storage after a reducing agent has been added is only a few percent of the total value.

Measurement of Terminal THM Concentration and Calculation of THM Formation Potential

These two parameters are discussed together because the measurement of InstTHM concentration is subtracted from the TermTHM concentration to yield the THMFP. To determine the TermTHM concentration, chlorine is reacted with trihalomethane precursors in a given sample in the dark under certain controlled conditions that affect yield and rate of formation of the trihalomethanes (discussed in Section III); the concentrations of the trihalomethane species produced are then measured. The conditions for this measurement are based on the conditions at the treatment plant under study and must be reproducible from sample to sample. "Precursor" is a mixture of organic chemicals, and the conditions chosen for their measurement will influence which fraction of the mixture is measured. Therefore, if any comparisons between samples are to be made, the measurement conditions *must* be the same, or a second variable, measuring a changing fraction of the precursor mixture, will be introduced into the experiment. Critical factors to be considered are: time of reaction; maintenance of a free chlorine residual; temperature; and pH. Each will be discussed as it relates to the evaluation of a given treatment process at a given water utility.

Effect of Time—

Although a single measurement of trihalomethane concentrations after a storage period of several days in a bottle under appropriate conditions can give a useful determination of the TermTHM concentration for that specified time, much more information can be gained from the reaction curves obtained by plotting trihalomethane concentration vs. time, i.e., the "rate curve." The rate curves obtained by periodic measurement of trihalomethane concentrations in properly stored water can be used to predict the trihalomethane concentrations at any given time after sampling.

In any system, the generation of the rate curve is recommended, at least initially, so that the nature of the reaction that occurs at a given location can be determined. Furthermore, if possible, periodic development of the rate curve is suggested to determine whether or not changes in precursor type are occurring. Figure 16 shows two hypothetical curves describing the rate of chloroform formation that might be expected for finished waters of distinctly different qualities after leaving typical water treatment plants.

Curves "A" and "B" in Figure 16 represent two extreme situations that might occur. Although at time "T" the chloroform concentrations are the same for two waters from the two treatment plants, the short-term chloroform concentration is greater in "Water A," and the long-term chloroform concentration is greater in "Water B." A "Water A" type curve would be expected where chloroform formation potential is relatively low, but the precursor present is of the type that reacts quickly under the given conditions, i.e., the final concentration of chloroform is reached

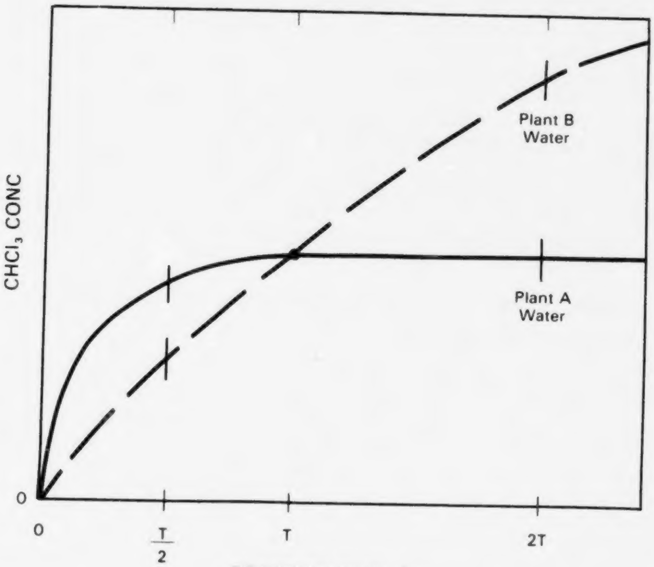

Figure 16. Formation of chloroform under widely different treatment plant conditions.

early. A "Water B" type curve would be expected where chloroform formation potential is high, but the reaction with chlorine is slow because of the nature of precursor or reaction conditions. Thus, these rate curves are more informative than a single chloroform determination performed at time "T," and a single measurement from each plant easily could be misinterpreted to mean that both situations were the same.

Good approximations of both curves can be obtained by selecting three or four points beyond time "0" (instantaneous value) such as "1/2T," "T," "2T" (as shown) where "2T" is equal to or slightly longer than the maximum distribution system residence time. With these added analyses, generating rate curves could be time consuming, especially if conditions are such that reactions are slow and the distribution system residence time is long. If developing a rate curve is beyond the capability of a utility, the time for storage during the determination of the TermTHM concentration should be the longest residence time in the distribution system, as this represents the most stringent condition for that utility.

Maintenance of Free Chlorine Residual—

In conventional water treatment practice in the United States, maintaining a free chlorine residual through the distribution system often is recommended or required. The continued reaction of precursor with chlorine to yield trihalomethanes depends on the maintenance of a free chlorine residual. Again, with chloroform as an example, the raw water curve presented in Figure 17 shows the abrupt cessation of chloroform production as the free chlorine residual became depleted. If a water utility maintained a free chlorine residual throughout the distribution system, the 24-hr and later chloroform concentrations from this test could be misleading. Thus, to avoid obtaining misleading results when evaluating systems where free chlorination is practiced, a chlorine residual measurement *always* must be performed at the time

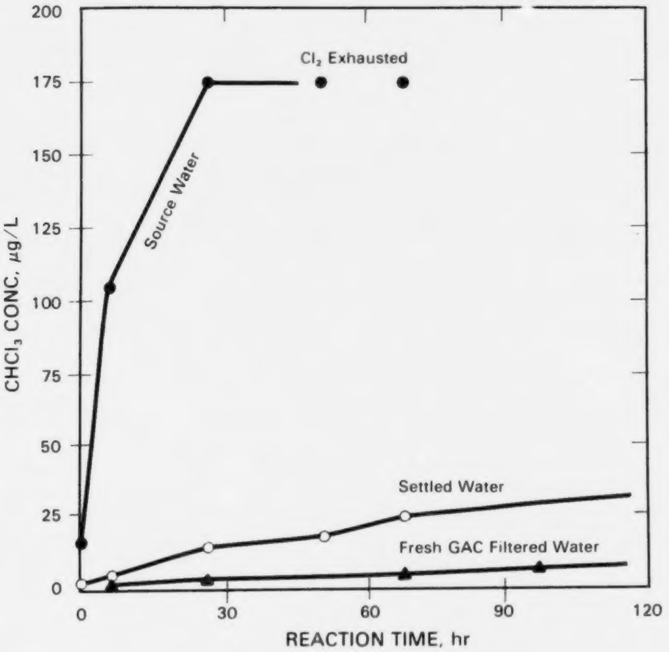

Figure 17. Effect of different treatment on chloroform formation. pH 7.0; 25°C (77°F); 8 mg/L chlorine dose.[15]

of the TermTHM analysis to ensure that a free chlorine residual is present. If insufficient free chlorine is in the water at the time of sampling to last through the test, chlorine must be added before sample storage.

Work at the USEPA-DWRD laboratory indicates that TermTHM concentrations are not influenced significantly by the amount of free chlorine present (Figure 12) as long as the concentration is above about 0.5 mg/L. This, which was not demonstrated with lower free chlorine residuals, may only be because the trihalomethane concentrations usually are limited by the amounts of precursors present. Because some uncertainty exists about the effect of chlorine concentrations on the reaction rate, however,[20,23-27] the starting free chlorine concentration used in the TermTHM determination should be nearly the same as the chlorine dose added at the treatment plant and possibly in the distribution system, if that dose is adequate to supply the required residual for the duration of the test.

Effect of Temperature—

Because temperature has a dramatic effect on rate of formation of trihalomethanes (Figures 2 and 3) and therefore on the yield at any given time, a need exists for close temperature control during the determination of the TermTHM concentration. At a waterworks, because temperature cannot be controlled but varies seasonally, selection of a sample storage temperature will depend on the experimental objective. For example, if the objective is to estimate *consumer exposure* to trihalomethanes throughout a year, a logical choice is the estimated average distribution system temperature, and this will vary depending on the time of the year the sample is collected. When the objective is to evaluate *precursor removal efficiencies* of a unit process, the same fraction of the precursor mixture must be measured during each test; therefore, the temperature must be maintained at a single value for all of the tests, regardless of the time of the year.

Effect of pH—

Selecting the pH for the controlled reaction during determination of the TermTHM concentration is less straightforward than that for reaction time and temperature. The variation of pH through an operating water treatment plant can be quite wide, and the variation is controlled operationally.

If the determination of only the TermTHM concentration and the THMFP for the finished water is desired, pH selection is not a problem; the samples should be stored at the finished water pH. Selecting pH is more difficult if a comparison is needed between the THMFP of the finished water with that of the raw water (or with water at any stage of treatment) to evaluate the success of a unit process in removing THMFP.

The analyst must be sure that the same fraction of the total precursor concentration, pH dependent (Figures 6 and 8), is reacting at each point of treatment evaluation and that the reaction rate of chlorine with the material, also pH dependent (Figure 8), is the same at each point. Thus, all of the samples from each of the various sampling points must be chlorinated and buffered at a single selected pH value before storage. Therefore, because the THMFP test is designed to measure the portion of the total precursor that is significant in a given water as it leaves a given treatment plant, the logical single reaction pH value is usually that of the finished water entering the distribution system, as it was with the choice of temperature. Recall that, as with temperature, when the objective is to evaluate *precursor removal efficiencies* of a unit process, the pH must be maintained at a single value in all tests. Therefore, the pH naturally occurring at the point in the treatment train where the sample was taken should be adjusted and buffered to the selected pH.

Summary of Procedures for InstTHM, TermTHM and THMFP

Procedures for measurement of these parameters have been discussed in terms of general concepts. Considerably more detail is given by Stevens and Symons[29] and analytical procedures are similar to those presented in the USEPA method 510.1 for Maximum Trihalomethane Potential (MTP). In summary, InstTHM is the measured trihalomethane concentration when the chlorine-precursor reaction was stopped by the addition of a chemical reducing agent at the time of sampling. TermTHM is the measured trihalomethane concentration after the reaction between precursors and free chlorine has been allowed to continue in a sealed container under specified conditions for a given time period.* THMFP is the arithmetic difference between TermTHM and InstTHM concentrations and represents the concentration of precursor that is unreacted, is present in the water at the time of the original sampling, and is of concern in a given situation.

Generation of the trihalomethane formation rate curve, although not always necessary, provides useful background information for plant and unit process evaluations. The rate of formation curve, when generated for finished water samples, provides a useful estimate of the trihalomethane concentration for any given time after the water leaves the treatment plant, an important factor. Section V discusses how these three parameters are specifically used to evaluate some example treatment plants.

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*Note, if any chemicals are added to the sample at the start of this determination, they must be free of bromide.

SECTION V
EXAMPLES OF TREATMENT EVALUATION TECHNIQUES

Two hypothetical examples will help to demonstrate the use of the InstTHM and TermTHM determinations and the calculated THMFP to estimate both consumer exposure to trihalomethanes resulting from the chlorination process and the efficiencies of various unit processes within the plant for removing precursor compounds during treatment. The efficiency of unit processes for removing chloroform or other trihalomethanes themselves can also be estimated.

These hypothetical examples should not be considered to be predictions of the success or failure of certain unit processes in a treatment train. The examples do serve to indicate the type of results that might be obtained when a plant is sampled for the measurement of InstTHM and TermTHM concentrations and THMFP concentrations calculated, and should help in understanding how this information is used for unit processes or whole plant evaluations as detailed in the treatment effectiveness research presented in Sections VI–VIII. For further information the reader is directed to Reference 29, where many other examples are given and their interpretations discussed more fully.

Simple Chlorination

The first example represents the simplest case, a water treatment plant with chlorination only. Figure 18 depicts the relative values for the parameters that might be obtained if analyses were conducted for the InstTHM concentration and TermTHM concentration at the source, "A," the plant clearwell, "B," and a theoretical point at the maximum residence time in the distribution system, "C." For simplification, the trihalomethanes are being discussed here as a group. Each bar could represent the single group index total trihalomethanes or any one of the individual species; or it could be subdivided horizontally into four bars of different heights to represent all commonly found trihalomethanes.

According to this bar graph, trihalomethanes were absent in the untreated source water, i.e., InstTHM was not found upon analysis of the source water, but the full THMFP was present and equal to the TermTHM concentration obtained experimentally. At the clearwell, some of the precursor measured as THMFP has reacted to form trihalomethanes (measured as InstTHM in the finished water) and has left a smaller remaining THMFP. The remaining THMFP, plus the InstTHM concentration, equals the TermTHM concentration determined originally on the source water. At point "C," the entire source water THMFP has reacted to give an InstTHM concentration identical to the TermTHM concentration.

No unit process at this plant effectively lowered either TermTHM or InstTHM concentrations. The practice of chlorination itself converted THMFP to InstTHM, thereby causing a decline in the THMFP concentration. In assessing the THMFP removal by any unit process, care must be taken to treat separately the removal of THMFP by conversion to InstTHM during chlorination and the removal of THMFP by the unit process itself. Only at a point closer to the treatment plant than the maximum length of the distribution system is the consumer exposed to trihalomethane concentrations (InstTHM) that are lower than the TermTHM concentration shown at point "C" in Figure 18. These two concepts will be discussed further in the more complex example presented below.

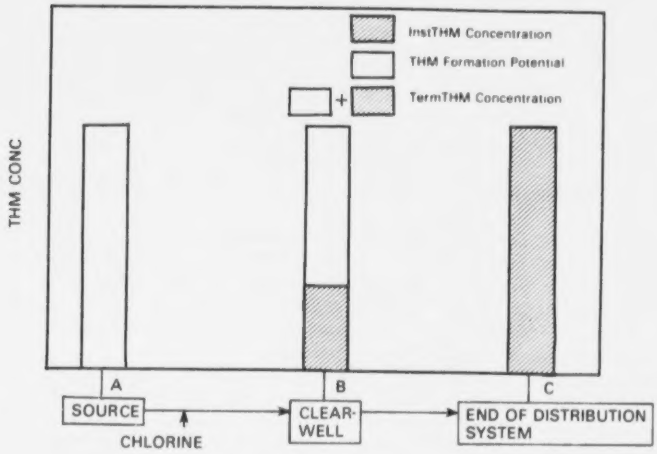

Figure 18. Trihalomethanes formed during water treatment by chlorination only.

Conventional Treatment

Finished Water TermTHM Concentration Reduction—

During conventional treatment with raw water chlorination (Figure 19) some trihalomethanes are formed during rapid mixing and throughout the following treatment stages in the presence of free chlorine. Thus, the InstTHM concentration increases as the water passes through rapid mixing, settling, and filtration, i.e., points "B," "C," and "D." Coagulation and settling do remove THMFP, i.e., precursor removal, so that parameter, as well as the TermTHM concentration declines from point "B" to "C." Filtration removes more precursor material that is associated with the carryover floc; therefore, the THMFP concentration declines slightly again from point "C" to "D," as does the TermTHM concentration. Recall that some of this THMFP concentration decline from point "B" to "C" to "D" results from conversion to InstTHM. (This is discussed more fully in the next subsection.) The remaining THMFP is converted by the free chlorine to trihalomethanes from point "D" to "E," and therefore, the InstTHM concentration determined for a sample taken at point "E" in distribution system equals the TermTHM concentration of the sample collected at point "D." Therefore, if the consumer farthest from the treatment plant is to receive water containing less trihalomethanes, the finished water TermTHM concentration must be lowered.

A concept that is important when attempting to evaluate the performance of unit processes and treatment schemes using the laboratory test technique relates to the difference in the behavior of trihalomethane formation in a test bottle as opposed to behavior in a treatment plant and distribution system. For example, source water and filtered water may be stored in test bottles and the TermTHM concentration determined on each sample, according to the method described earlier in Section IV. The difference in these two concentrations of TermTHM indicates the removal of trihalomethane precursors during treatment. Moving the point of chlorination from the source water to the filtered water in the treatment plant will *not* necessarily, however, cause the fully equivalent decline in the TermTHM concentration in the finished water after the change in chlorination practice at the plant although some lowering of the TermTHM concentration usually will occur because of precursor

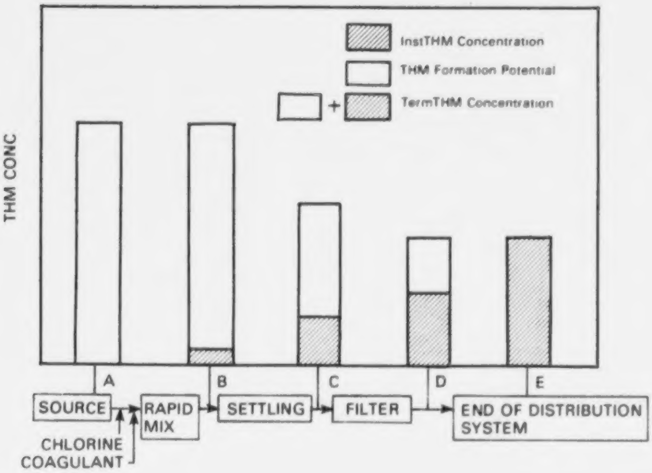

Figure 19. Trihalomethanes formed during conventional treatment with source water chlorination.

removal during treatment. The full source water TermTHM concentration, as measured in the test bottle, will *not* be realized in the distribution system, even when the *source* water is chlorinated in the treatment plant; compare points "A" and "E" in Figure 19. This is because the test bottle is a closed system with intimate mixing of precursor and free chlorine for the duration of the test, and the treatment plant is not. That is, some precursor is removed "across" the unit process in the treatment plant before it is able to react with the free chlorine, even when source water chlorination is practiced. Therefore, as noted above, InstTHM and TermTHM measurements "across" unit processes give accurate information about process effectiveness for trihalomethane and precursor removal, but in themselves, they do not reflect the exact degree of trihalomethane control to be expected by movement of the point of chlorination from one place to another in the treatment plant.

Actually moving the point of chlorination in a treatment plant and measuring the influence on the TermTHM concentration in the finished water is the best method of establishing what effect precursor removal before chlorination will have at that site. Some approximation may still be obtained, however, by conducting some "bottle" experiments at the plant and interpreting the data according to the example in Figure 20.

In this hypothetical case with chlorination at the rapid mix during routine operation (Figure 20), "Amount B" of the source water precursor is removed by sedimentation, "Amount C" is converted to InstTHM during flocculation and settling, and "Amount A" remains as THMFP after settling. Moving the chlorination point to the settling basin effluent would allow *some portion* of "Amount C" precursor to be settled out ("Amount X" in Figure 20) before it is chlorinated, because, after the point of chlorination is moved, the reaction of chlorine with this precursor would not be "competing" with settling for "Amount C." Further, moving the point of chlorination is not likely to influence the fraction [B/(A+B)] of *unreacted* precursor (A+B) that was removed, because that fraction is already being successfully settled out without reacting with the chlorine that was present during routine operation. Therefore, the TermTHM concentration would decline *only* by whatever "Amount X" of "Amount C" would be in a given situation.

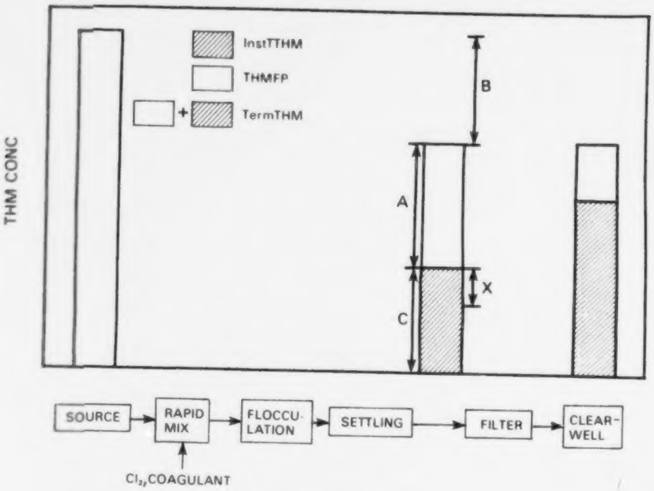

Figure 20. Example of using "bottle" data for predicting performance of settling on precursor removal.

The decline in finished water TermTHM concentration cannot be *exactly* predicted from the data collected in the bottles because the rate at which trihalomethanes are being formed, the rate at which precursors are being settled, and the mix of precursors being influenced by each reaction would not be known. Clearly, the decline will not equal "Amount B" (Figure 20). Some *approximations* can be made from bottle experiments, however, because the "fraction" of precursor converted to trihalomethanes during passage through the unit process under study during routine conditions [C/(C + A) in Figure 20] can be evaluated in laboratory experiments, and the magnitude of this "fraction" influences the potential for success.

For example, the lower this "fraction," the less the chance of success will be for lowering the finished water TermTHM concentration by chlorination after the precursor removal unit process. In that case, free chlorine and precursor are reacting slowly, so the precursor that is settling is not involved significantly in the trihalomethane formation reaction, causing the point of chlorination to be of little importance. Of course, the opposite is also true. In situations where a high "fraction" of precursor is converted to InstTHM during passage through a unit process when free chlorine is present, the chance of success for improving precursor removal by delaying chlorination until later in the treatment train is higher, as more precursor material could be precipitated if the rapid conversion to InstTHM were prevented from "competing" with the settling process.

Another factor that must be considered in judging the potential for success of any plan to lower finished water TermTHM concentrations (by enhancing precursor removal through moving the point of chlorination) is the degree of precursor removal in the unit process under study. If in the example shown in Figure 20, "Amount B" were a small percentage of the unit process influent, "Amount A + B + C," then the chance for success in lowering the finished water TermTHM by moving the chlorine point downstream would be small, no matter what the magnitude of the C/(C+A) fraction.

The same concepts may be applied even when some InstTHM is present in the influent to the unit process under study. In this case, "Amount C" would be the *increase* in InstTHM concentration "across" the unit process under study. The remainder of the analysis would be carried out as outlined above.

As mentioned previously, the concentration of THMFP can be lowered in two ways: either TermTHM concentrations can be lowered because of precursor removal or precursor can be converted to InstTHM. Hypothetically, in Figure 21 for example, when the chlorination point was moved from the source water to the settling basin effluent, more THMFP was present in the clearwell after the move than before, even though the TermTHM concentration declined a little. This results from the decline in InstTHM concentration that occurs because of the shorter trihalomethane formation reaction time before the clearwell—a shorter time caused by the change in chlorination practice. Further, under routine operation (source water chlorination), a large decline in THMFP concentration occurred from the settling basin effluent to the clearwell because of the increase in InstTHM concentration, even though the TermTHM concentration only declined slightly. Care must be taken, therefore, when interpreting THMFP concentration data.

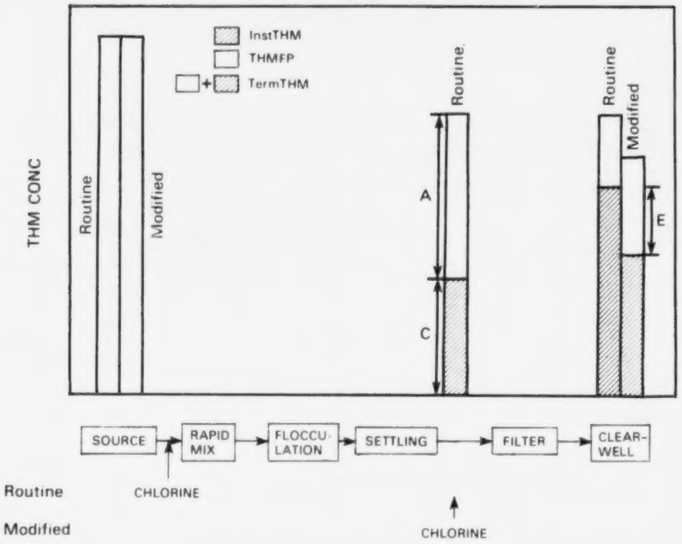

Figure 21. Decline of InstTHM and TermTHM concentrations with change of point of chlorination.

Finished Water InstTHM Concentration Reduction—

The previous subsection detailed methods of anticipating finished water TermTHM concentration declines during treatment alternatives because this will reduce InstTHM concentrations at the extremities of the distribution system. Some success may, however, accrue from a treatment modification even if the finished water TermTHM concentration does not decline much.

In the example in Figure 21, the finished water TermTHM concentration did not decline much after the point of chlorination was moved, but, because of the delay in chlorination, the finished water InstTHM concentration was reduced by "Amount E" (Figure 21). Therefore, although the total trihalomethane concentration at the end of the distribution system was not lowered significantly, many consumers nearer the treatment plant might receive substantially lower total trihalomethane concentrations in their drinking water because of the change in treatment practice. This benefit should not be overlooked.

The development of a trihalomethane formation rate curve will help quantify these benefits. Recall that, according to the Trihalomethane Regulation,[3] as much as 75 percent of the compliance samples are to be collected from the central part of the distribution system where this benefit would occur.

Other Considerations

During such evaluations, the TermTHM concentration of the source water should be monitored as a control to ensure that any change in finished water TermTHM concentration is not caused by a change in the characteristics of the source water. Table 2 shows how the trihalomethane precursor concentrations changed during a 12-month period in the Ohio River at Cincinnati. The change in the bromine-containing trihalomethane species concentrations indicated a change in the bromide content of the river, as well as the change in total trihalomethane concentrations. Note, although the samples were not buffered, the changes in pH over the study period were not great and therefore did not influence the data excessively.

TABLE 2. INFLUENCE OF SEASON ON TRIHALOMETHANE FORMATION POTENTIAL* IN THE OHIO RIVER, 1977-1978

Month	Number of samples	Geometric mean (G_m) Trihalomethanes, μg/L				G_m TTHM, μg/L
		$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	
July	2	153	41	6.5	NF†	200
August	4	120	43	8.3	<0.1	171
September	4	108	44	9.3	0.1	161
October	5	120	33	5.5	<0.1	158
November	3	106	30	7.3	<0.1	143
December	3	144	29	5.6	NF	179
January	2	103	23	8.0	0.2	134
February	3	89	27	8.8	0.1	125
March	4	147	17	1.6	NF	166
April	5	115	21	2.3	NF	138
May	4	109	32	5.2	NF	147
June	4	92	35	5.0	0.1	132
July	4	109	47	13	1.1	171
Max.		153	47	13	1.1	200
Min.		89	17	1.6	NF	125
Spread		64	30	11.4	1.1	75

*3 days storage; 25°C (77°F); samples not buffered, pH range 5.9 to 7.0.
†None found.

Further, the possibility exists that precursor concentration may change in the distribution system because debris on the pipe walls might act as precursor. If this is occurring, the TermTHM concentration measured in the finished water would be lower than the InstTHM concentration measured at the corresponding point in the distribution system. In the five places where this has been investigated, however, good agreement was obtained between these two parameters (References 30 and 31 and the unpublished 1976 National Organics Monitoring Survey).

Finally, investigators planning to conduct the type of studies outlined above must be aware of the need to repeat sampling frequently enough to overcome the inherent problems of variability in the trihalomethane analytic results. To be able to assess accurately changes in treatment performance, multiple samples may be needed to provide a data base large enough to make the observed concentrations statistically significant. Variability also occurs from trial to trial, necessitating several repeats of the experiment to ensure confidence in the findings.

SECTION VI
TREATMENT TECHNIQUES TO REMOVE TRIHALOMETHANES (InstTHM)

Background

The proposed[10] and the promulgated Trihalomethane Regulation[3] contain a Maximum Contaminant Level (MCL) for the total trihalomethane concentration; the decision as to what treatment strategy is best to meet the MCL in a given location is left up to the individual utility, with approval of the Primacy Agency.

Because the general reaction of free chlorine with precursors to form trihalomethanes is:

$$\begin{array}{c}\text{FREE}\\\text{CHLORINE}\end{array} + \begin{array}{c}\text{PRECURSORS}\\\text{(HUMIC SUBSTANCES)}\\\text{AND BROMIDE}\end{array} \rightarrow \text{TRIHALOMETHANES} + \begin{array}{c}\text{OTHER}\\\text{BYPRODUCTS}\end{array}$$

three treatment approaches are possible. These are:

1) treatment to remove trihalomethanes (InstTHM) after formation
2) treatment to remove trihalomethane precursors (THMFP), and
3) the use of disinfectants other than free chlorine.

Each of these techniques has been discussed in the literature;[32-36] in Sections VI, VII, and VIII, the research information for each of these approaches will be updated with:

- controlled experiments, both by USEPA's Drinking Water Research Division and by others reporting in the open literature;
- case histories, where available; and
- the advantages and disadvantages.

Note, although the Trihalomethane Regulation[3] establishes an MCL for total trihalomethanes, for many of the treatment techniques studied, the four common trihalomethane species behave differently. Therefore, where the data are available, the performance of the unit processes for the removal of the individual species during the experiment, as well as the removal of the arithmetic sum of their concentrations, total trihalomethanes (TTHM) will be reported.

Oxidation

General Considerations—

The possibility of removing trihalomethanes by oxidation, using either ozone or chlorine dioxide as the oxidant, was investigated by USEPA-DWRD in-house. An attempt was made to stimulate the oxidation of trihalomethanes during ozonation by adding ultra-violet light energy.

Experimental Results—

Ozone—For these studies, a 3.7-cm (1.5-in) diameter glass counterflow ozone contactor was fabricated. Ozone (O_3) was generated by a Welsbach Model T-408® generator using "aviator's breathing" grade oxygen. The ozone-oxygen gas mixture was dispersed through a fritted glass sparger in the bottom of the contactor. Applied ozone concentrations were determined by an iodometric method.[37] In an effort to maximize contact between the ozone-oxygen mixture and the water, a small, high-speed, propeller mixer was positioned just below the water surface within the column. The propeller caused almost complete dispersion of the rising bubbles. Even at an applied ozone dose of 25 mg/L (5- to 6-minute contact time) attempts to remove trihalomethanes from Cincinnati tap water were unsuccessful (Table 3).

TABLE 3. OXIDATION OF TRIHALOMETHANES, CINCINNATI TAP WATER OZONATION. (Gas to water ratio 0.5 to 1 [V/V] 5- to 6-minute contact time.)

Sample	Applied O_3* dose (mg/L)	Trihalomethanes (µg/L) $CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM (µg/L)
Tap water	0	10	9	6	1	26
Mixer only	0	11	10	7	1	29
Oxygen only	0	12	10	7	1	30
Air only	0	12	8	4	0.8	25
Ozone only	25	11	10	7	0.9	29
Mixer + O_2	0	11	9	6	0.5	27
Mixer + air	0	12	8	6	1	27
Mixer + O_3	25	11	9	6	0.9	27

*Applied dose, continuous flow studies, mg/L =

$$\frac{\text{mg } O_3}{\text{standard liter of gas } (O_3 + O_2)} \times \frac{\text{standard liter gas } (O_3 + O_2)}{\text{minute}} \times \frac{\text{minute}}{\text{liters of water}}$$

Chlorine Dioxide—This study examined chlorine dioxide (ClO_2) prepared by reacting technical grade (80 percent pure) sodium chlorite ($NaClO_2$) with sulfuric acid, air-stripping the chlorine dioxide from solution, and trapping the gas in nitrogen-purged distilled water. Analyses for chlorine and chlorine dioxide were made using a DPD procedure.[38] At dosages up to 10 mg/L and storage for 2 days, chlorine dioxide, like ozone, was ineffective in removing the trihalomethanes already present in the water (Table 4).

TABLE 4. OXIDATION OF TRIHALOMETHANES, CINCINNATI TAP WATER, CHLORINE DIOXIDE TREATMENT[39] (Temperature = 25°C [77°F]; pH = 7.4-7.5)

ClO_2 dose (mg/L)	Contact time (hours)	Trihalomethanes (µg/L) $CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM (µg/L)
0	0	26	15	10	1.1	52
7	24	26	18	14	NF*	58
7	49	24	16	11	NF	51
0	0	40	22	13	NF	75
10	42	39	22	17	NF	78

*None found.

Ozone/Ultra-Violet Radiation—Glaze et al. studied the use of ozone in combination with ultra-violet radiation (O_3/UV) as a treatment process for removing micropollutants from drinking water.[40] Table 5 summarizes the results obtained for the disappearance of chloroform and bromodichloromethane using a laboratory-scale, sparged, stirred-tank, semi-batch, photochemical reactor.

TABLE 5. HALF LIVES* FOR CHLOROFORM AND BROMODICHLOROMETHANE[40] (Ozone dose rates = 0.775 mg/L min†; UV intensity = 0.20 Watts/L†)

Compound	Matrix	Purging	Ozonolysis	Photolysis	Ozone/UV
$CHCl_3$	PW‡	462	NMD**	139	3.25
	LLW§	729	22,400	753	86.6
$CHBrCl_2$	PW	495	NMD	61.9	6.3
	LLW	2660	NMD	116	53.3

*Minutes.

†Midrange of the experimentally investigated values.

‡Specially prepared laboratory water low in organic carbon concentration and ozone demand (pH 6.5 to 7.0).

**No measurable decline.

§Natural water from local lake (pH 8.1).

The first order reaction rates are expressed in terms of half-life, that is, the time required under the reaction conditions given for any concentration of contaminant to be lowered to one-half of its initial value. Ozone alone had little or no influence on the two trihalomethanes tested; further, ultraviolet radiation alone (photolysis) destroyed chloroform and bromodichloromethane very slowly, half lives of 61.9 to 753 minutes. In comparison, the combination treatment was much more effective, lowering the concentrations of these two trihalomethanes to one-half of their initial values in 3.25 to 6.3 minutes for the specially prepared water in the laboratory and 53.3 to 86.6 minutes in the lake water.

Discussion—

Of these three oxidation techniques, the combination of ozone and ultra-violet radiation was the only one that showed any promise for the removal of trihalomethanes that have already been formed. This approach is considered to be still in the research stage, however, and is not ready in a practical treatment application.

Aeration

General Considerations—

Among the several factors influencing the effectiveness of removing organic compounds from water by aeration are contact time, ratio of air to water, temperature, vapor pressure, and solubility of the contaminant(s). Although contactor design will be seen later to be very critical to unit process efficiency and cost, the last two variables can be useful for estimating the feasibility of aeration. For example, Henry's law states that when dissolved, the partial pressure of a compound over a solution varies directly with its concentration in the liquid phase. The concentration of the contaminant in the gas phase, therefore, is proportional to its concentration in the liquid phase. Henry's law constant, sometimes called the partition coefficient, can be calculated from experimental data by dividing the concentration of the contaminant in the air by its concentration in water at equilibrium. This constant can be estimated from the special case conditions where the concentration of the contaminant is at saturation in both the liquid and vapor phase, causing the partial pressure of the contaminant to be equal to the vapor pressure of the pure material.[41,42] Thus, Henry's law constant, H, becomes:

$$H \propto \frac{P_v}{S} \qquad \text{[Eq. 1]}$$

where: P_v = vapor pressure of the pure liquid and
S = solubility of the contaminant in water.

Thus, lower compound solubility and higher vapor pressure (volatility) result in a higher Henry's law constant. By conversion of partial pressure units to concentration in the gas phase, a dimensionless Henry's law constant:

$$H = \frac{C_a}{C_w} \qquad \text{[Eq. 2]}$$

where: C_a = concentration of the compound in air in μg/L and
C_w = concentration of the compound in water in μg/L

can be calculated.

The following analysis will show how aeration theory can be applied to the analysis of operating aeration systems; the experimental data in the next subsection will be analyzed by these techniques.

Theoretically, a counterflow aeration tower is the most efficient system with regard to air use to achieve a given treatment goal. Therefore, the performance of a theoretically perfect "ideal" tower will be discussed to form a basis for comparison of actual experimental treatment results given later.

In theory, when a counterflow aeration tower is operated ideally, the concentration in the water of the contaminant to be removed is in equilibrium with the concentration of the contaminant in the air at any point in the system. Further, according to Equation 2, the concentration in the water is equal to the concentration in the air divided by the Henry's law constant, at any point in the aerator. Because the concentration of the contaminant in the air coming into the bottom of the system is zero, in a "perfect" tower the concentration of the contaminant in the water must also be zero, to satisfy the definition of an ideal column being at equilibrium at every point. Thus, the perfect system would remove all of the contaminant in question.

The operation of a counterflow aeration column or tower can be portrayed graphically by plotting the concentrations of the contaminant in the air and water at any series of points through the depth of the column.

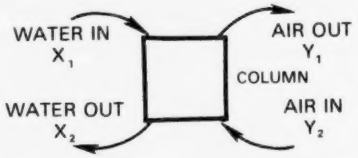

Figure 22. Schematic of ideal counterflow aeration system.
x_1 = initial concentration of the contaminant in the water
x_2 = final concentration of the contaminant in the water
y_1 = final concentration of the contaminant in the air
y_2 = initial concentration of the contaminant in the air

Calculating a mass balance based on Figure 22, loss of contaminant in water equals gain of contaminant in the air, yields:

$$(x_1 - x_2)\, W_v = (y_1 - y_2)\, A_v \qquad \text{[Eq. 3]}$$

where: W_v = water volume
A_v = air volume.

In the perfect column that is at equilibrium throughout, from Equation 2 at any point:

$$\frac{C_a}{C_w} = \frac{y_1}{x_1} = H \qquad \text{[Eq. 4]}$$

Therefore at the top of the column $y_1 = (H)(x_1)$.

Substituting this in Equation 3 yields:

$$(x_1 - x_2)\, W_v = [(H)\,(x_1) - y_2]\, A_v \qquad \text{[Eq. 5]}$$

Because both x_2 and y_2 are zero in the ideal system, Equation 5 becomes

$$(x_1)\, W_v = (H)\,(x_1)\, A_v \qquad \text{[Eq. 6]}$$

Cancelling yields:

$$\frac{W_v}{A_v} = H \text{ or } \frac{A_v}{W_v} = 1/H \qquad \text{[Eq. 7]}$$

This means that in the *perfect* system, the *minimum* air to water ratio that will achieve complete removal for the contaminant in question is the reciprocal of its Henry's law constant.

Henry's law constants have recently been estimated for low concentrations to be 0.152 for chloroform, 0.095 for bromodichloromethane, 0.035 for dibromochloromethane, and 0.024 for bromoform (Werner, USEPA, Cincinnati, OH, personal communication, 1980). Experience has shown that compounds with Henry's law constants greater than 0.05 could be removed relatively easily by aeration.[43] Therefore, the possibility of trihalomethane treatment by aeration was considered. This concept was supported by a 1975 study[42] that showed chloroform lost to the atmosphere when water was held in open vessels and by a 1976 report[44] of chloroform being dissipated from a flowing stream that had accidentally been contaminated by a chloroform spill.

As noted previously, in an ideal counterflow tower, the minimum air to water ratio that will produce complete removal of a given contaminant is the reciprocal of the Henry's law constant for that contaminant. More air would be wasteful (it would not be at equilibrium with the liquid phase), and less air would not achieve complete removal.

The Henry's law constants noted above for the four trihalomethanes were used to construct an equilibrium diagram (Figure 23). These data show the equilibrium concentration in air for a given concentration in water for the four trihalomethanes. The slope of these curves (H), proportional to the ease with which the contaminant can be removed by aeration in a countercurrent system, indicates that bromoform would be the most difficult of the four trihalomethanes to remove by aeration.

Graphically from the curves (Figure 23) or by calculation from H (as above), the theoretical minimum air to water ratios required to achieve complete removal in a perfect tower are 6.7:1, 10.2:1, 28:1, and 41:1 for chloroform, bromodichloromethane, dibromochloromethane, and bromoform, respectively.

In graphical form, the actual performance of an aeration tower is called the operating line. For the trihalomethanes, the equilibrium lines shown in Figure 23 are theoretical operating lines for perfect towers operating at the theoretical minimum air-to-water ratios for accomplishing complete removals of the respective compounds. The degree of removal achieved by lower air-to-water ratios can be determined as shown in Figure 24.

Here, as above, for chloroform with a Henry's law constant of 0.15, an air-to-water ratio of 6.7 to 1 is needed to achieve complete removal of the contaminant in a perfect tower. Starting from an arbitrary influent concentration in the water of 100 µg/L, lower air-to-water ratios produce the theoretical operating lines as shown, remembering that equilibrium is always achieved at the top of an ideal column (concentration in water is 100 µg/L and on the equilibrium line). Operating lines are

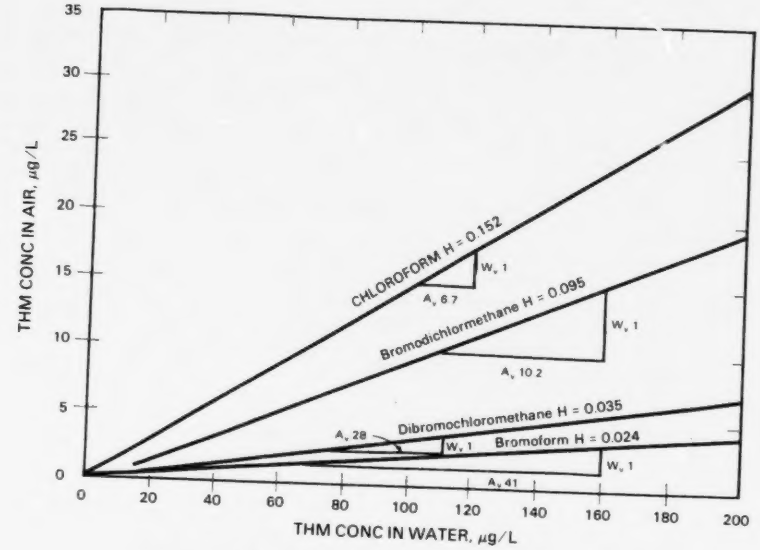

Figure 23. Equilibrium lines for four trihalomethanes.

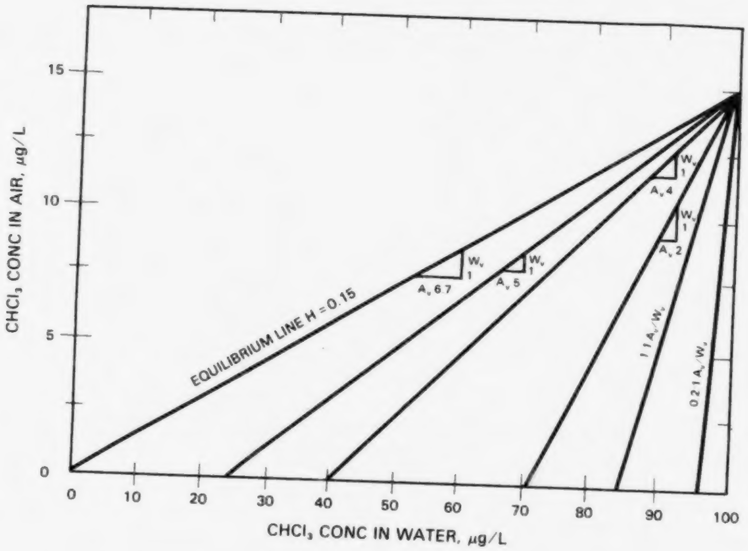

Figure 24. Examples of the performance of an ideal counterflow tower at air to water ratios less than the theoretical minimum for complete removal.

then drawn with the slopes 1/5, 1/4, 1/2, 1/1, 5, corresponding to air-to-water ratios of 5:1, 4:1, 2:1, 1:1, and 0.2:1, respectively. Extending the lines to the x intercept (concentration of chloroform in air would be zero at the bottom of a counterflow column) gives the concentration of chloroform remaining in the water for each of these air-to-water ratios in an *ideal* column for this compound. From the corresponding effluent concentrations, a plot of percent chloroform remaining versus air-to-water ratio will produce a curve for ideal tower operation against which any field aeration data can be measured. Designs that approach the theoretical performance should be desirable. This type of comparison was also suggested by Singley et al.[45]

Figure 25 is a plot of the theoretical optimum performance curves for each of the four trihalomethanes at various air-to-water ratios developed by use of the technique shown in Figure 24. The relative difficulties of removing each of the trihalomethanes compared with that of chloroform (the easiest) can be clearly seen by comparing the theoretical minimum air-to-water ratios required to achieve a given percent removal of each compound, as shown in this figure.

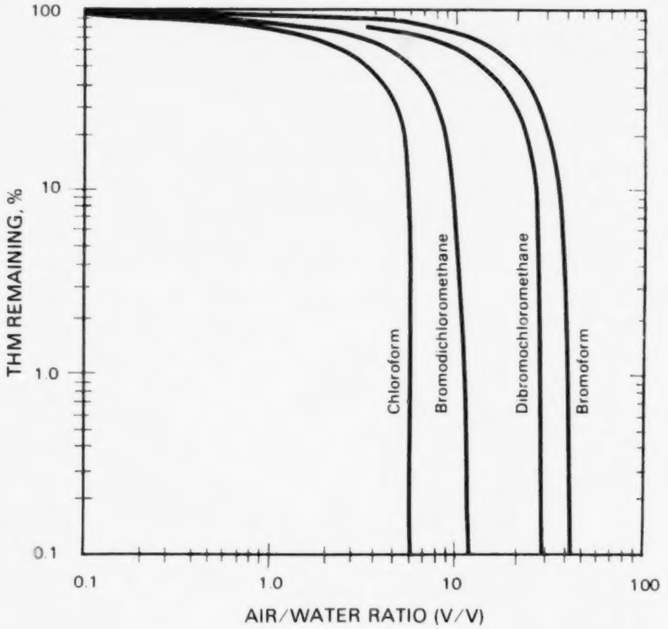

Figure 25. Performance of ideal counterflow tower for removal of four trihalomethanes.

Very importantly, however, no actual aeration system is perfect, so less than 100 percent removal always occurs, even with air-to-water ratios much higher than the theoretical minimum. This occurs because numerous design factors influence the *rate* of mass transfer from the liquid phase (water) to the gas phase (air). Departure from the equilibrium condition provides the driving force that causes the contaminant to move across the air-water interface. This driving force is greater when conditions are not near equilibrium and becomes small as equilibrium is approached. Thus, aeration system design becomes exceedingly important in facilitating mass transfer if the low theoretical minimum air-to-water ratios to achieve good removal are to be approached in actual practice. Some important design parameters to be considered are liquid or gas flow rates, selection of packings (tower) to optimize surface area, and transfer unit height (contact time).

Although in application temperature cannot be controlled, it must be taken into account in both design and perhaps even selection of aeration as a unit process. Temperature influences not only mass transfer rates, but the magnitude of Henry's law constant (H) and, therefore, the equilibrium conditions as well. Clearly, freezing and the entrapment of airborne contaminants (dirt) can also be a problem, especially in towers.

Principles for design of efficient aeration systems have been developed in the chemical engineering field. For example, these principles have recently been synthesized into a design approach for countercurrent aeration towers in drinking water applications by Kavanaugh and Trussel.[46] These actual system design considerations and procedures are considered beyond the scope of this Research Report, however, and will not be treated in depth here.

A review of the limited available data showing actual removals of trihalomethanes by aeration follows. These laboratory, pilot, and field performance results will then be compared with the results of the theoretical optimum treatment developed above. Batch reactor experiments will be presented first, followed by continuous-flow experiments.

Experimental Results—

Quiescent Standing—To investigate the volatility of trihalomethanes under quiescent conditions, an open vessel containing Cincinnati tap water, left standing at room temperature (about 25°C [77°F]), was sampled periodically for Inst THM. A nearly complete loss of trihalomethanes occurred after 3 days, even though some trihalomethanes were being produced during the experiment by the free chlorine residual (Table 6).

TABLE 6. NET* LOSS OF TRIHALOMETHANES FROM AN OPEN VESSEL, CINCINNATI TAP WATER†

Time of standing (hours)	Trihalomethanes (μg/L)				TTHM (μg/L)	Percent TTHM removal
	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$		
0	16	4	4	2	26	—
6	13	4	2	NF‡	19	27
24	7	3	1	NF	11	58
48	3	1	<1	NF	4+	83
72	1	<1	NF	NF	1+	94

*Some trihalomethane produced during the experiment by the free chlorine residual.
†Room temperature about 25°C (77°F).
‡None found.

Diffused-Air Aeration—Using Louisville, Kentucky, tap water, Weil studied diffused-air aeration in a 500 mL batch reactor.[47] By using various air flow rates and exposure times, he created various air-to-water ratios. Removals of TTHM varied from 25 to 80 percent depending on the air-to-water ratio (Table 7).

The Contra Costa County Water District has also investigated diffused-air aeration for the removal of trihalomethanes in batch reactors.[20] In the first test, treated water samples were aerated in a 4-liter stainless steel beaker using a porous stone diffuser (Kordon Mist A-501®) with an air flow of 0.5 L/min. For the second test, a 6-cm (2.5-in) diameter glass column 0.9 m (3 ft) long was used for the aeration studies. Because of the high concentration of bromoform (which has a lower

TABLE 7. DIFFUSED-AIR AERATION STUDIES,* LOUISVILLE, KY, TAP WATER[47]

Air to water ratio (V/V)	Aeration time (minutes)	Trihalomethanes (μg/L)				TTHM (μg/L)	Percent TTHM removal
		$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$		
Control	0	17.3	12.3	5.8	NF†	35.4	0
1.25:1	2.5	11.9	9.5	5.1	NF	26.5	25
2.5:1	5	11.2	8.8	4.9	NF	24.9	30
5:1	10	7.9	6.7	4.2	NF	18.8	47
Control	0	11.9	11.7	7.6	0.7	31.9	0
2.5:1	2.5	7.5	8.2	6.4	0.6	22.7	29
5:1	5	5.8	5.9	5.1	0.4	17.2	46
10:1	10	2.8	3.2	3.9	0.5	10.4	67
Control	0	24.6	19.7	8.2	NF	52.5	0
3.75:1	2.5	14.1	12.8	6.4	NF	33.3	37
7.5:1	5	7.9	8.3	5.1	NF	21.3	59
15:1	10	3.4	3.5	3.5	NF	10.4	80
Control	0	10.5	9.5	8.8	1.1	29.9	0
5:1	2.5	6.2	5.0	6.1	1.0	18.3	39
10:1	5	5.1	3.0	4.6	0.7	13.4	55
20:1	10	3.6	1.2	2.0	0.5	7.6	75

*Batch reactor.
†None found.

estimated Henry's law constant compared with that of chloroform) in this water, removal of the trihalomethanes would be expected to be difficult when compared with that of Louisville's tap water in which chloroform is the dominant trihalomethane.[47] The data in Table 8, when compared with that in Table 7 (both being batch reactors), show this to be the case. As one example, at a 15 to 1 air-to-water ratio, 86 percent of the chloroform was removed from Louisville's tap water, whereas at the same air-to-water ratio, only 38 percent of the bromoform was lost from Contra Costa's drinking water. The two systems were not exactly comparable, however, as shown by the removal of dibromochloromethane—57 percent in the Louisville study and 40 percent at Contra Costa, both at a 15 to 1 air-to-water ratio.

For the DWRD in-house study, a countercurrent aeration column was fabricated from a 3.7-cm (1.5-in) diameter glass tube, 0.9 m (3 ft) long, with a fritted glass diffuser. At an air-to-water (volume-to-volume) ratio common to water treatment aerator designs for controlling taste and odor problems (1 to 1), the chloroform concentration in Cincinnati tap water was not significantly changed from that of the control, although a decline in the concentration of bromodichloromethane did occur (Table 9). Increasing the air-to-water ratio to 8 to 1 yielded a 52 percent TTHM concentration decline, and a further increase to 20 to 1 showed an 84 percent decrease. For comparison purposes, a conventional activated sludge wastewater treatment plant is designed with about an 8 to 1 air-to-water ratio, and the gas-to-water ratio in the purging step in the trihalomethane analysis[3] is approximately 44 to 1 when operated as a batch system. Although the ratio of chloroform to total trihalomethane concentrations are not exactly the same in Cincinnati and Louisville tap water, 0.77 versus 0.42 (average of four experiments), the percent removals of total trihalomethanes were similar at similar air-to-water ratios, Table 7[47] and Table 9, even though the data in Table 7 were from a batch reactor.

TABLE 8. DIFFUSED-AIR AERATION STUDIES,* SEPTEMBER 1977, CONTRA COSTA COUNTY WATER DISTRICT[20]

Approximate air-to-water ratio (V/V)	Height of water column (cm)	Height of water column (in)	Aeration time	Trihalomethanes (μg/L) $CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM (μg/L)	Percent TTHM removal
OPEN CONTAINER TEST									
Control sample	—	—	—	<1	3	24	239	266	—
1:1	14	5.5	10 min	2	12	49	199	262	1.5
4:1	14	5.4	30 min	2	11	43	160	216	19
8:1	13	5.3	60 min	1	10	38	130	179	32
19.1	13	5.2	120 min	1	9	30	75	115	57
COLUMN TEST									
Control sample	—	—	—	2	4	28	196	230	—
12:1	45	18	1 hr	3	2	18	140	163	29
15:1	38	15	2 hr	2	1	15	122	140	39
6:1	90	36	1 hr	2	3	24	171	200	13
6:1	80	32	2 hr	2	3	22	159	186	19
Control sample	—	—	—	3	4	33	229	269	—
9:1	90	36	4 hr	3	2	19	139	163	39
Control sample	—	—	—	5	18	84	189	296	—
22:1	90	36	8 hr	3	7	44	133	187	37

*Batch system.

TABLE 9. REDUCTION OF TRIHALOMETHANE CONCENTRATIONS IN WATER BY DIFFUSED-AIR AERATION,* CINCINNATI TAP WATER

Air†-to-water ratio (V/V)	Chlorine residual (mg/L)	Trihalomethanes (μg/L)				TTHM (μg/L)	Percent TTHM removal
		$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$		
Control	1.3	99	24	5	NF‡	128	—
1:1	1.2	101	5	5	NF	111	13
8:1	1.2	45	13	3	NF	61	52
12:1	1.2	33	7	<1	NF	40+	69
16:1	1.2	19	8	3	NF	30	77
20:1	1.1	16	5	3	NF	21	84

*Countercurrent flow.
†Activated carbon filtered compressed air.
‡None found.

Tower Aeration—Rook studied the removal of chloroform in a 4-m (12.4-ft) high cascading countercurrent aerator filled with crosswise arranged racks of plastic tubing.[26] His data showed a 50 percent removal of chloroform at a calculated air-to-water ratio of 3.2 to 1.

Houel et al. studied the removal of chloroform spiked into water by air stripping in a countercurrent tower having a cross section of 60 by 45 cm (23 by 18 in) and a total packing depth of 4 m (14 ft).[48] The air supply was metered and capable of delivering a maximum of about 35 m^3/min (1,250 cfm). Water loading rates up to 27 m^3/day (5 gpm) were used. Two packing materials were used: Type A, egg crate style; and Type B, a proprietary product, Munters Plasdek®, Code CF-1DA, inclined wavy PVC sheets. The results in Table 10 show that at these very high calculated air-to-water ratios, chloroform was very effectively removed.

TABLE 10. TOWER AERATION FOR THE REMOVAL OF CHLOROFORM FROM CHLOROFORM-SPIKED WATER[48]*

Variable	Run number					
	1	2	3	4	5	6
Packing type†	A	A	A	B	B	B
Calculated air-to-water ratio (V/V)	6100:1	7700:1	9400:1	1800:1	2500:1	2600:1
Initial $CHCl_3$ concentration (μg/L)	843	843	843	536	638	536
Final $CHCl_3$ concentration (μg/L)	<0.1	<0.2	<0.1	13.2	1.6	<0.2
Percent $CHCl_3$ removal	>99.98	>99.97	>99.98	97.5	99.8	>99.96

*Countercurrent flow.
†See text for description.

McCarty reported on a study at Water Factory 21 in Orange County, California, in which tower aeration was included as part of the treatment scheme.[43] In this study, both large cross-flow stripping towers and smaller countercurrent decarbonators were studied. The two stripping towers were each 63 m (210 ft) long by 19 m (62 ft) wide and contained 7.6 m (25 ft) of polypropylene splash-bar packing. Six fans were included per tower, each 5.5 m (18 ft) in diameter. They provided 990 m^3/sec (2 × 10^6 cfm) of air, or about 3,000 m^3 air/m^3 of water (calculated air-to-water ratio) at design capacity. The two stripping towers were designed to treat 0.66 m^3/sec (15 mgd) of flow.

The two decarbonators were designed to treat 0.22 m^3/sec (5 mgd) of flow. Each was 2 m square (6.5 ft) and contained 2.4 m (8 ft) of polyethylene packing. The total volume of media in the decarbonators was only 19 m^3 (670 ft^3) compared with 18,000 m^3 (634,000 ft^3) in the stripping towers. Each decarbonator had a blower designed to provide 22 m^3 air/m^3 water applied (calculated air-to-water ratio). Although the concentrations of the trihalomethanes were quite low, making the calculation of a percent removal somewhat suspect, the data (Table 11) show good removals.

Wood et al. studied the removal of trihalomethanes, both spiked into and naturally occurring in Miami, Florida, tap water, in a 2.7-m (9-ft) high countercurrent tower 0.3 m (1 ft) square.[49] The packing media was 1.3-cm (0.5 in) diameter PVC pipe on 8-cm (3 in) centers. The flow through the tower was 160 m^3/day (30 gpm) and was distributed over the cross-section of the tower by nine showerheads. To study increasing air-to-water ratios, the water was recycled to provide multiple passes. An induced draft was provided by a 4.2-m^3/min (150-cfm) fan, resulting in a calculated 38 to 1 air-to-water ratio when the fan was on. Studies were made both with and without the fan operating. The data in Table 12 show that in this particular instance, the fan did not aid in the stripping of chloroform, a finding similar to that shown in Table 11.[43]

Studies sponsored by the American Water Works Association Research Foundation employed a 15-cm (6-in) diameter countercurrent column packed with various depths of 0.6-cm (1/4-in) interlocked ceramic saddles, Intalox®.[50] Various water flows and forced-draft air flows were used to study different air-to-water ratios. The data in Table 13 show the improvement of aeration with increased depth at a constant calculated air-to-water ratio, as well as the positive influence of increasing the air-to-water ratio at a constant depth.

The difference between the initial chloroform concentration and TTHM concentration indicates the presence of bromine-containing trihalomethanes in this water. The average ratio of chloroform concentration to total trihalomethane concentration was 0.76 for the five tests. Under these circumstances, the percent removal for TTHM should be lower than for chloroform because of the difficulties in stripping the bromine-containing trihalomethanes. This was not shown in three of these five tests, although the concentration of the bromine-containing trihalomethanes might not have been high enough to significantly influence the data.

Two other studies demonstrated the positive influence of air-to-water ratio and tower height on removal of trihalomethanes. In another test during the Miami, Florida, study, Wood et al. investigated the effect of increasing air-to-water ratio on the removal of the four trihalomethane species spiked into Miami tap water by passing the water through the tower several times.[49] Although the air-to-water ratio was not known, it increased incrementally with each water pass. The same tower was used as described previously. The data in Table 14 confirmed two previously noted conclusions: one, that the increase of air-to-water ratio with each pass had a positive influence on the stripping of trihalomethanes; and two, that bromoform, as expected, is more difficult to remove by aeration than is chloroform. The air-to-water ratio needed to obtain 61 percent bromoform removal was twice that needed to obtain 61 percent chloroform removal.

TABLE 11. REMOVAL OF TRIHALOMETHANES BY AIR STRIPPING AT WATER FACTORY 21[43]

Contaminant	Cross flow stripping towers						Counterflow decarbonator, Induced draft		
	Induced draft			Natural draft					
	$\frac{A^*}{W}$	Concentration† (μg/L)	Percent removal (95% CI‡)	$\frac{A^*}{W}$	Concentration† (μg/L)	Percent removal (95% CI)	$\frac{A^*}{W}$	Concentration† (μg/L)	Percent removal (95% CI)
$CHCl_3$	3000:1	1.1	83 (70-91)	UNK§	4.1	79 (64-87)	22:1	10	79 (70-85)
$CHBrCl_2$	3000:1	—	—	UNK	—	—	22:1	4.1	85 (76-91)
$CHBr_2Cl$	3000:1	—	—	UNK	0.8	82 (76-87)	22:1	1.7	71 (49-84)

*Air-to-water ratio (V/V).
†Influent to stripping process given as the geometric mean concentration.
‡Confidence interval.
§Unknown.

TABLE 12. REMOVAL OF TRIHALOMETHANES IN MIAMI, FLORIDA, TAP WATER[49]*

Compound	Initial concentration (μg/L)	Run 1 (Natural draft)			Run 2 (Induced draft)		
		Final concentration (μg/L)	Percent removal	Air-to-water ratio†	Final concentration (μg/L)	Percent removal	Air-to-water ratio†
$CHCl_3$	106	48	55	UNK‡	52	51	38:1
$CHBrCl_2$	113	73	35	UNK	67	41	38:1
$CHBr_2Cl$	62	45	27	UNK	40	36	38:1
$CHBr_3$	8.4	7.5	11	UNK	6.5	23	38:1
TTHM	289	173	40	UNK	165	43	38:1

*Countercurrent flow; tower aeration, 2.4 m (8 ft) high.
†Volume to volume.
‡Unknown.

TABLE 13. REMOVAL OF TRIHALOMETHANES AT NORTH MIAMI BEACH, FLORIDA[50][*]

Variable	Run number				
	1	2	3	4	5
Packed bed depth					
meters	1	2.1	2.5	2.1	2.1
feet	3.3	7	8.3	7	7
Calculated air-to-water ratio (V/V)	10:1	10:1	10:1	32:1	40:1
$CHCl_3$					
Initial concentration (μg/L)	29	26	23	27	27
Final concentration (μg/L)	15	9.4	7.1	6.2	5.9
Percent removal	48	64	69	77	78
TTHM					
Initial concentration (μg/L)	40	35	29	35	33
Final concentration (μg/L)	22	12	9.3	7.0	5.9
Percent removal	45	66	68	80	82

[*] Countercurrent flow, forced draft; tower aeration; water temperature = 27°C (81°F).

TABLE 14. REMOVAL OF TRIHALOMETHANES SPIKED INTO MIAMI, FLORIDA, TAP WATER[49][*]

Pass	Relative air-to-water ratio	Percent removal				
		$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM[†]
1	x[‡]	61	69	55	39	47
2	2x	91	86	75	61	74
3	3x	97	95	90	86	89
4	4x	99	98	95	90	93
5	5x	99+	99	97	93	95

[*] Countercurrent flow; tower aeration, natural draft (air-to-water ratio cannot be calculated).

[†] Dominated by bromoform that was spiked at a concentration about seven times that of the other trihalomethanes.

[‡] Unknown.

In another test, one of the cooling towers for the USEPA Environmental Research Center's air conditioning system in Cincinnati was used to examine the effects of countercurrent-induced draft-packed tower aeration on trihalomethane removal. Cincinnati tap water was passed through one side of the tower and samples were collected at the midpoint and the bottom, approximately 2 m and 4 m (6 ft and 12 ft), respectively, both with and without the fan in operation. This tower was designed for over 12,000 m^3/day (2,200 gpm) of recirculated flow, but the flow for this study was limited to about 3,000 m^3/day (550 gpm) for the single-pass study. The low flow through a part of the unit prevented an estimate of an air-to-water ratio, but the improvement in trihalomethane removal with increasing tower depth is shown in Table 15.

Discussion—

The data presented above can now be compared among studies and against the theoretical optimum system described in the General Considerations subsection.

TABLE 15. TRIHALOMETHANE REMOVAL IN A COOLING TOWER,* CINCINNATI TAP WATER†

	Trihalomethanes (μg/L)				TTHM (μg/L)	Percent TTHM removal
	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$		
Influent						
Run 1	44	21	7	1	76	—
Run 2	48	24	10	1	84	—
Midpoint—2 m (6 ft)						
Induced draft						
Run 1	4	1	1	1	7	91
Run 2	3	1	1	NF‡	5	94
Natural draft						
Run 1	10	5	4	1	20	74
Run 2	8	4	3	1	16	81
Bottom—4 m (12 ft)						
Induced draft						
Run 1	3	1	1	NF	5	93
Run 2	3	1	1	NF	5	94
Natural draft						
Run 1	6	2	2	1	11	86
Run 2	7	3	2	1	13	85

*Unknown air-to-water ratio.
†Countercurrent flow.
‡None found.

Figure 25 is based partly on the assumption that the initial concentration of a contaminant does not influence the percent remaining for a given air-to-water ratio. To verify this concept, the data from the multi-pass experiment reported in Table 14[49] were reanalyzed. The data in Figure 26 show that for chloroform, in this experiment, the same percentage of the chloroform concentration present in the water at the start of each pass was remaining at the end of that pass, for all four passes through the column. Therefore, the percent remaining after each pass was independent of the starting concentration (lower at the beginning of each pass) and thus, a single "perfect counterflow column" curve can be used for the analysis in Figure 25. Similar data were also obtained for the other trihalomethanes measured in this experiment.

Having verified the "universality" of Figure 25, all data were plotted on the same graph, Figure 27, to compare the performance of all the systems with data on chloroform removal where air-to-water ratios were available with the operation of a perfect counterflow system. Figure 27 can be used to compare system efficiencies. The farther a given datum point is to the right of the perfect counterflow column line, the less effectively air is being used for a given percent chloroform remaining.

In inefficient cases, mass transfer (water to air) must be improved to accomplish more effective use of air. As described earlier, this can be done by changing design parameters such as liquid or gas flow rates, selecting packings (for towers), and increasing contactor height. Any of these changes may affect the cost of the system or its operation, and therefore, cost benefits realized by using less air must be weighed against cost increases brought by improvement in system mass transfer efficiency.

From Figure 27, in general, the best removals of chloroform were by countercurrent towers (greater than 90 percent) although air use was relatively inefficient; more efficient use of air was observed in batch diffused air experiments, but actual chloroform removals were poorer (approximately 50 percent). For this

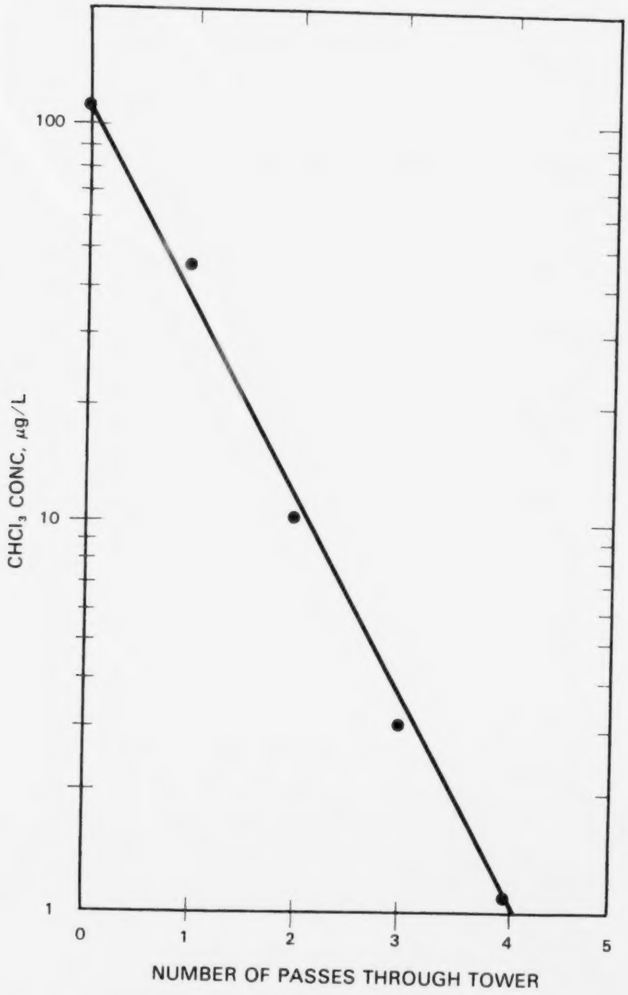

Figure 26. Miami, Florida, tower aeration study.[49]

application, diffused air systems generally require higher air-to-water ratios (because of poorer mass transfer efficiency) than do countercurrent towers to accomplish the same treatment goal. When required, scaleup of the diffused air systems to achieve percent removals greater than 90 percent by increasing air-to-water ratios may prove to be difficult. Conversely, tower design improvements may result in more efficient use of air for the higher percent removal examples shown in Figure 27. Studies may show that diffused air systems are appropriate when required removals of trihalomethanes are minimal whereas towers may be generally preferred for utilities requiring larger percentage removals.

In summary, aeration is a feasible approach to trihalomethane removal, with the difficulty of removal increasing with molecular weight from chloroform to

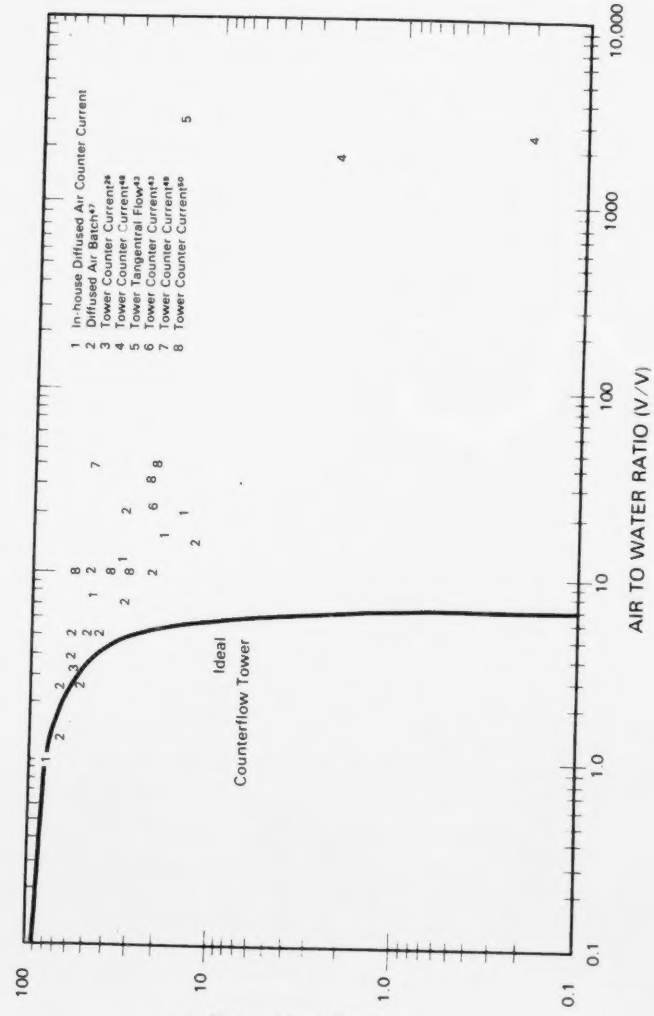

Figure 27. Comparison of chloroform removal for various experimental systems with ideal tower operation.

bromoform. A utility considering aeration for trihalomethane control should consider the feasibility on the basis of known sound aerator design principles. Because of variations among utilities, such as degree of treatment required, mixture of trihalomethanes present, temperature, and other water quality considerations, this should be followed by pilot study verification at that location.

Adsorption

Powdered Activated Carbon (PAC)—

General Considerations—To determine what degree of removal of dissolved organic material can be effected by adsorption, an isotherm test is usually run. The adsorption isotherm is the relationship between the amount of substance adsorbed and its concentration in the surrounding solution at equilibrium. The adsorption isotherm consists of a curve plotted with residual concentration of the solute in solution on the "x" axis and the amount adsorbed per unit weight of adsorbent on the "y" axis. Thus, any point on the line gives the adsorption capacity or loading at a particular concentration in solution. With activated carbon adsorption from dilute solutions, such as trihalomethanes in drinking water, a logarithmic plotting according to the empirical Freundlich equation,

$$x/M = kC^{1/n} \qquad \text{[Eq. 8]}$$

where: x = amount of substance adsorbed, calculated from original and equilibrium concentrations, C_o and C_f,

M = weight of activated carbon, and

k and n are constants; k is the intercept at $C_f = 1$ ($\log C_f = 0$) and $1/n$ is the slope of the line

usually yields a straight line over the concentration ranges for trihalomethanes usually found in drinking water.

Data points required to construct the adsorption isotherm are usually obtained by applying varying doses of PAC to replicate samples of a solution of the solute in question (a trihalomethane) in water. These samples are held in suitable containers to prevent losses. After equilibrium is achieved, no further change in solute concentration occurs. The activated carbon is then separated from the liquid sample, and residual dissolved solute concentrations are measured. The calculated values of X/M are plotted against respective C_f values on log/log coordinates.

Using closed containers and under controlled conditions with 2 hours of contact, Dobbs and Cohen determined the adsorption isotherms for the trihalomethanes in distilled water using ground Filtrasorb® 300.[51]* Adsorption isotherms can be used to calculate the required PAC dose needed to reduce a contaminant concentration from some given influent concentration to some target effluent concentration. Using Figure 28 as an example, to reduce the chloroform concentration from 150 μg/L to 75 μg/L, the required PAC dose is calculated as follows. The equilibrium "loading" (X/M) on the adsorbent at the final chloroform concentration of 75 μg/L (arrow) is about 0.38 μg chloroform adsorbed per mg of PAC (Figure 28). Because (150 μg/L − 75 μg/L) = 75 μg chloroform/L that must be adsorbed, 75/0.38 = 197 mg PAC/L is required. As this is a very high PAC dose, it indicates the generally poor adsorbability of chloroform by activated carbon.

Figure 29, in which the adsorption isotherms for all four common trihalomethanes are shown together, indicates the increased adsorbability of the bromine-containing trihalomethanes. Using the same example as above for bromoform, 15 mg powdered

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*Manufactured by Calgon Corporation, Pittsburgh, PA 15230. Hereafter Calgon Corporation products are either designated Filtrasorb® 200 or F-200, Filtrasorb® 300 or F-300, or Filtrasorb® 400 or F-400.

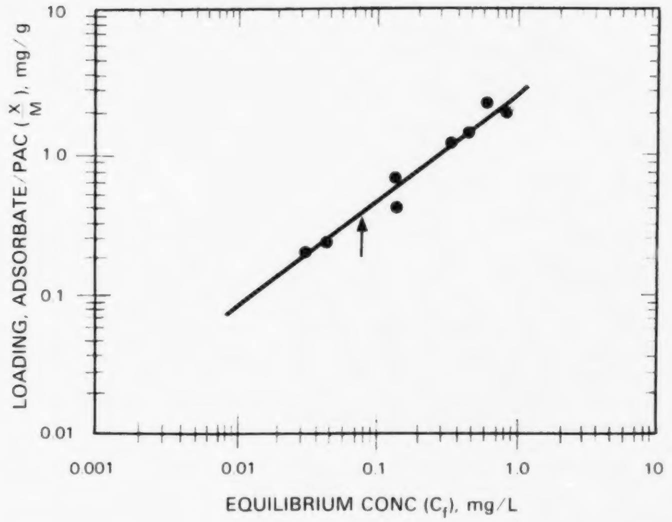

Figure 28. Adsorption isotherm for chloroform with F-300.[51]

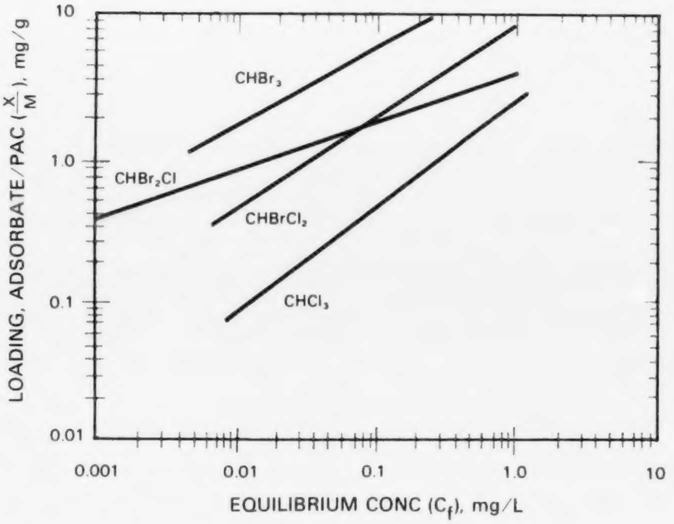

Figure 29. Adsorption isotherm for four trihalomethanes with F-300.[51]

Filtrasorb® 300/L would be required to lower a concentration of 150 μg/L to 75 μg/L, or only 7.6 percent of the PAC dose required for the same amount of chloroform removal.

The above discussion assumes that equilibrium is reached during the normal water treatment process where PAC is applied. Even though the rate of adsorption (approach to equilibrium) is typically rapid when PAC is used, normally measured in minutes to hours, equilibrium may not always be reached at utilities using a short contact time. This kinetic effect would reduce the effectiveness of this treatment technique.

Additionally, other solutes present in the water being treated may compete for "active sites" on the adsorbent, and disinfectant residuals may influence adsorbent qualities. Adsorption capacities for different activated carbons will also vary. These effects complicate extrapolations from published isotherm data to actual water treatment practice, as will be seen below.

Experimental Results—In one study, where the trihalomethanes occurred naturally, Weil exposed Louisville, KY, tap water containing little free chlorine residual, 0.12 mg/L, to various doses of PAC in 1-liter mixed, open containers, and determined the residual trihalomethane concentrations after various exposure times.[47] His data (Table 16) confirm that at least 50 mg/L PAC was needed to bring about 50 percent removal of total trihalomethanes. As expected, the percent removal of bromodichloromethane and dibromochloromethane was higher than the percent chloroform removal for each PAC dose and exposure time. This, again, shows the increased adsorbability of the bromine-containing trihalomethanes. The adsorption isotherm of the 60-minute exposure data for chloroform compares fairly well with the results of Dobbs and Cohen,[51] the slope being similar, but the line displaced upward (Figure 30). Note that the use of open containers may have contributed to the loss of the solute attributed to adsorption.

In another jar test study, Hoehn et al. chlorinated simulated lake water containing 3 mg humic acids/L.[52] To avoid the complicating factor of the presence of a chlorine residual, in one experiment they dechlorinated the water before adding the PAC (lower curve, Figure 31). These data, when transferred to an adsorption isotherm format, produced a typical adsorption isotherm, although displaced from the data of Dobbs and Cohen[51] (Figure 32). Two factors that may have influenced these data are the type of PAC used in the Hoehn et al.[52] study and the presence of floc.

In another experiment, these investigators allowed the chlorine residual, 10 mg/L, to remain when the PAC was added to the test vessels.[52] The increase in chloroform concentration for the same PAC dose (upper curve, Figure 31) is likely to be caused by the influence of the chlorine residual present during this type of test. The residual chloroform concentration increased because chloroform was being formed by the reaction of precursor and free chlorine during the 30-minute exposure in the jars, as evidenced by the increase in chloroform concentration at the zero PAC dose. At other PAC doses, however, the increase in chloroform concentration could be influenced by: 1) the alteration of the surface of the activated carbon by the free chlorine so it was less able to adsorb chloroform (McGuire et al.[53]); 2) the PAC itself because it was acting as a chloroform precursor or introducing associated precursor; 3) a combination of both factors; or 4) the reason noted above, even though the PAC would tend to lower the chlorine residual. Nevertheless, the resulting adsorption isotherm does not deviate from the adsorption isotherm using data collected in the absence of a chlorine residual (Figure 32, page 58), which indicates that the reaction of free chlorine and precursor in the water is probably the most important factor in this case.

Many water treatment plants are designed to add PAC to water containing both coagulant and chlorine residual for taste and odor control. Therefore, studies of this type are typical of some situations encountered in the field. For example, before July 1975, the Cincinnati Water Works added chlorine and alum to Ohio River water

TABLE 16. TRIHALOMETHANE CONCENTRATIONS IN POWDERED ACTIVATED CARBON (PAC) EXPERIMENTS,[47] LOUISVILLE, KY, TAP WATER*

PAC dose (mg/L)	Exposure time (minutes)	Trihalomethanes†							
		$CHCl_3$ (μg/L)	Percent removal	$CHBrCl_2$ (μg/L)	Percent removal	$CHBr_2Cl$ (μg/L)	Percent removal	TTHM (μg/L)	Percent TTHM removal
0 (Control)	0	35.2	—	12.3	—	0.7	—	48.2	—
	5	30.3	—	10.3	—	1.1	—	41.7	—
	15	31.8	—	10.2	—	0.7	—	42.7	—
	30	30.2	—	10.5	—	0.7	—	41.4	—
	60	29.4	—	8.7	—	0.5	—	38.6	—
25	0	35.2	0	12.3	0	0.7	0	48.2	0
	5	26.3	13	7.2	30	0.3	73	33.8	19
	15	24.1	24	5.9	42	0.3	57	30.3	29
	30	23.2	23	5.3	50	0.2	71	28.7	31
	60	19.2	35	3.9	55	0.1	80	23.2	40
50	0	35.2	0	12.3	0	0.7	0	48.2	0
	5	25.0	17	4.9	52	0.2	82	30.1	28
	15	18.1	43	3.1	70	0.1	86	21.3	50
	30	17.7	41	2.7	74	0.1	86	20.5	50
	60	15.5	47	2.1	76	0.1	80	17.7	54
100	0	35.2	0	12.3	0	0.7	0	48.2	0
	5	17.4	43	2.8	73	0.1	91	20.3	51
	15	13.2	58	1.4	86	0.0	100	14.6	66
	30	10.1	67	1.0	90	0.0	100	11.1	73
	60	9.7	67	0.8	91	0.0	100	10.5	73

*Free chlorine residual = 0.12 mg/L.

†No bromoform found.

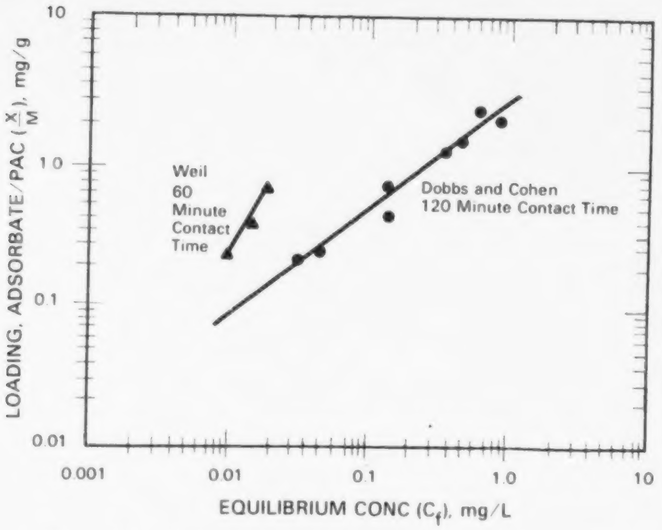

Figure 30. Comparison of chloroform adsorption isotherms from Weil[47] and Dobbs and Cohen.[51]

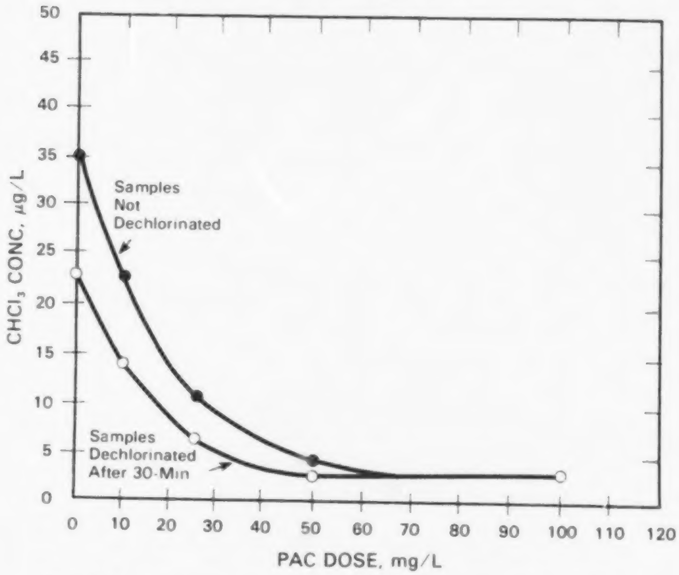

Figure 31. Treatment of simulated lake water with PAC. pH 7.9; 27°C (81°F); 3 mg/L humic acid
Treatment:
a. 10 mg/L prechlorination.
b. coagulation/flocculation/sedimentation
c. activated carbon; 30-min contact; pH 6.7
d. filtration[52]

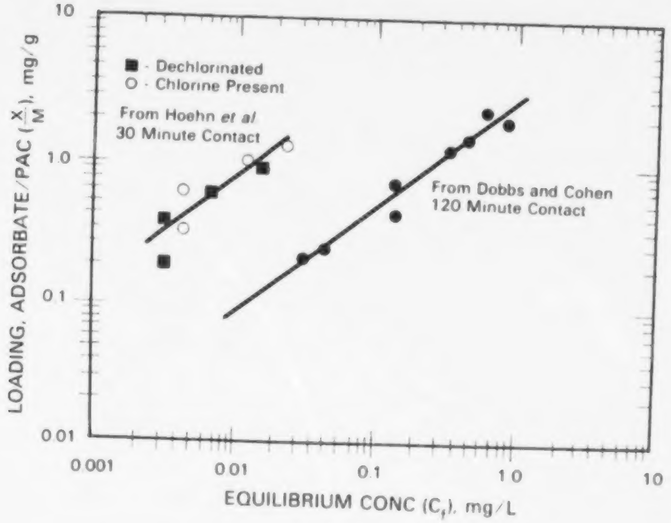

Figure 32. Comparison of the adsorption isotherms for chloroform from Hoehn et al.[52] and Dobbs and Cohen.[51]

before 2 days' storage in off-stream reservoirs. For taste and odor control, PAC was often added at the rapid mix in the presence of free chlorine residual and coagulant. Although this practice is common, it should be avoided where possible and in new designs. In an in-house study of this water, PAC was added to the water samples, mixed at 100 rpm for 2 minutes and 50 rpm for 5 minutes, settled for 30 minutes, centrifuged at 1,500 rpm (480 gravities) for 20 minutes, decanted, and analyzed for trihalomethanes. The data in Table 17 show that doses of PAC far higher than conventionally used for taste and odor control were required to obtain significant

TABLE 17. REDUCING TRIHALOMETHANE CONCENTRATIONS IN CHLORINATED OHIO RIVER WATER USING POWDERED ACTIVATED CARBON (PAC)*

PAC† dose (mg/L)	Trihalomethanes (μg/L)				TTHM (μg/L)	Percent TTHM reduction
	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$		
0	64	9	2	NF‡	75	—
1	52	7	1	NF	60	20
2	53	7	1	NF	61	19
4	51	7	<1	NF	58+	23
8	51	8	1	NF	60	20
16	48	8	<1	NF	56+	25
32	45	6	1	NF	52	31
64	35	4	<1	NF	39+	48
100	30	2	<1	NF	32+	58

*Alum and chlorine added and water stored off-stream in open reservoirs for 2 days.
†Watercarb®, manufactured by Husky Industries, Dunnellon, FL 32630.
‡None found.

removals. The data in Figure 33 show the relationship between the reaction of free chlorine and PAC and the adsorption of chloroform by PAC. Converting these chloroform data to an adsorption isotherm format produced a very atypical pattern (Figure 34) which suggests that the presence of the free chlorine residual had a significant influence on the adsorption phenomenon in this case.

Singley et al.[54] in North Miami Beach, Florida, and Carns and Stinson[55] at the East Bay Municipal Utility District in California attempted to evaluate the use of PAC for the adsorption of trihalomethanes. None of the trials were unusually successful, and all had at least the complicating problem of the presence of chlorine residual. Because some polyelectrolytes used in water treatment can act as trihalomethane precursors (Feige et al.[56]), investigators conducting jar tests or full plant experiments where these materials are present should control for their possible influence.

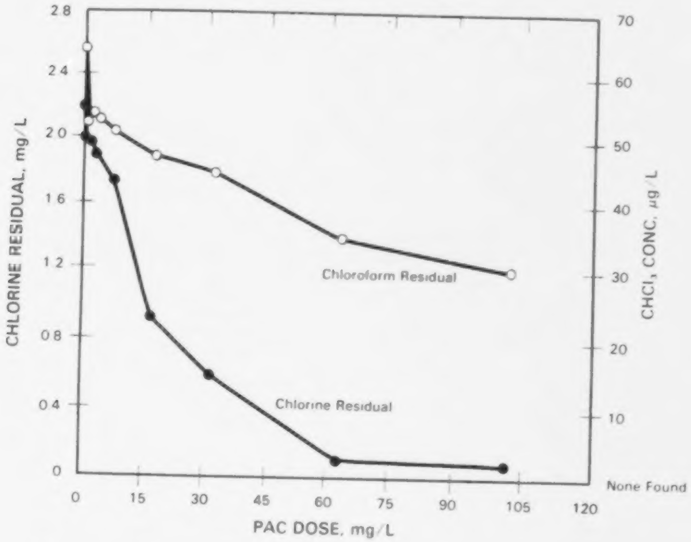

Figure 33. Effects of powdered activated carbon on the removal of chloroform from chlorinated Ohio River water.
Conditions:
a. Ohio River water + chlorine, alum
b. pH 6.6–6.8
c. 2.2 mg/L initial free chlorine residual
d. PAC added
2 min rapid mix
5 min slow mix
30 min settling
centrifuge at 480 gravities

Discussion—The summary curve (Figure 35) comparing the four studies reported above shows that the three studies conducted in the absence or near absence of a chlorine residual produced typical adsorption isotherms, although separated from each other. This is contrasted with the abnormal adsorption isotherm resulting from the study suspected to be influenced by the presence of a free chlorine residual. None of the experiments[47,51-55] or the in-house study showed that PAC was particularly

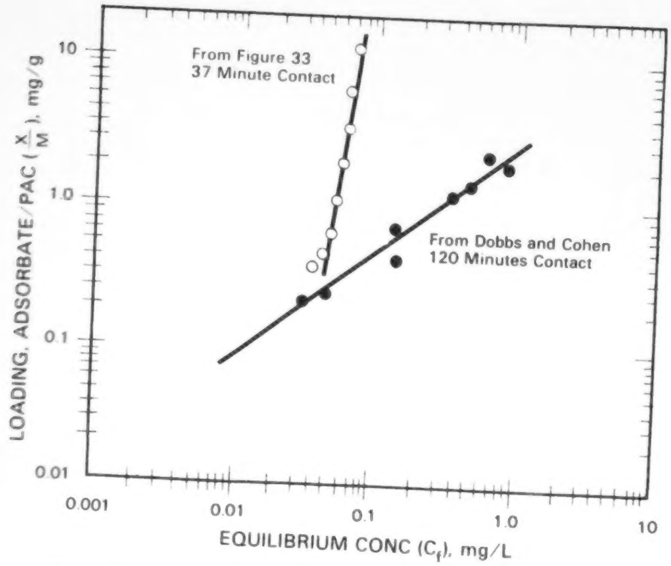

Figure 34. Comparison of adsorption isotherms for chloroform from a USEPA-DWRD in-house study and Dobbs and Cohen.[51]

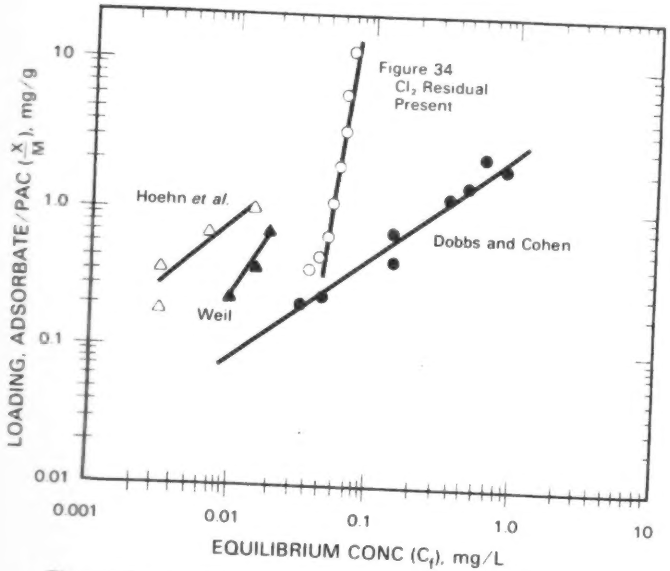

Figure 35. Summary of four studies (References 47,51,52, and a USEPA-DWRD in-house study) of the adsorption of chloroform on powdered activated carbon.

effective for the removal of chloroform. The bromine-containing trihalomethanes were much more adsorbable, however, and if they dominate the trihalomethane mixture in a given location, treatment with PAC might be considered as an effective treatment.

Granular Activated Carbon (GAC)—

General Considerations—GAC adsorption systems used in drinking water treatment typically use stationary beds with the liquid flowing downward through the adsorbent. Under these conditions adsorbed material accumulates at the top of the bed until the amount adsorbed at that point reaches a maximum. The maximum amount of a contaminant that can be adsorbed on activated carbon occurs when the adsorbed material is in equilibrium with the concentration of the contaminant in solution surrounding the adsorbent. For any given concentration of material in the liquid phase, the "loading on" or "capacity of" the activated carbon at equilibrium can be determined from the appropriate adsorption isotherm, as discussed above. When the adsorbed material is in equilibrium with the influent concentration, the adsorbent is "loaded" to capacity and that portion of the bed is "exhausted." In an ideal "plug flow" operation, the exhausted zone moves downward with time in service until the entire adsorbent bed is exhausted. This is shown graphically in Figure 36 where the shaded area represents the exhausted activated carbon and the clear area is the remaining fresh activated carbon in the lower portions of the bed. Figure 36 also represents the corresponding breakthrough profile of the contaminant in solution with time. The effluent concentration (C_{OUT}) remains near zero until the exhausted zone of the GAC reaches the bottom of the column and then abruptly increases to the influent concentration when the entire column is exhausted. Thus, the effluent concentration is equal to the influent concentration when the column is exhausted or at equilibrium, and ideally, therefore, the time to exhaustion of an adsorber can be predicted from isotherm test information.

For a given situation, the time to reach exhaustion can be estimated by knowing the influent contaminant concentration, the approach velocity (to calculate mass loading), the adsorber bed depth, the density of the adsorbent, and the equilibrium loading from an adsorption isotherm. This estimation assumes a constant influent concentration of contaminant and neglects the influence of competitive adsorption. For example, assume an influent chloroform concentration of 100 μg/L, a 5 m/hr (2 gpm/ft^2) approach velocity, a 0.9-m (3-ft) bed depth, and an adsorbent density of 490 kg/m^3 (30 lb/ft^3). According to Figure 28, at exhaustion ($C_i = C_f$), the loading on or capacity of the adsorbent would be 0.49 mg/g or g/kg.

For a 0.09 m^2 (1 ft^2) cross-section of this bed 2 gal/min × 1,440 min/day × 3.78 L/gal = 10,886 L/day pass through. Multiplying by the chloroform concentration, 10,886 L/day × 100 μg/L, yields 1.09 g/day of chloroform applied to the 0.09 m^2 (1 ft^2) cross-section. This cross-section, 0.9 m (3 ft) deep, contains 0.08 m^3 (3 ft^3) of media. Converting this to weight yields 41 kg (90 lb) of adsorbent. Therefore, the days required to "load" this adsorbent to equilibrium is:

$$\text{Days of operation} = \text{Total weight of adsorbent} \times \text{equilibrium loading/daily load} \qquad \text{[Eq. 9]}$$

$$\text{Days of operation} = (41\ \text{kg})\ (0.49\ \text{g/kg})/1.09\ \text{g/day}$$
$$18.4\ \text{days}$$

Thus, an estimated 18.4 days would be required to exhaust this bed. The data in Table 18 are examples of these calculations for a GAC adsorber with a 10-minute empty bed contact time (EBCT)* and an approach velocity of 5 m/hr (2 gpm/ft^2).

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*Empty bed contact time (EBCT) equals "empty bed volume" divided by the "flow rate" through the bed.

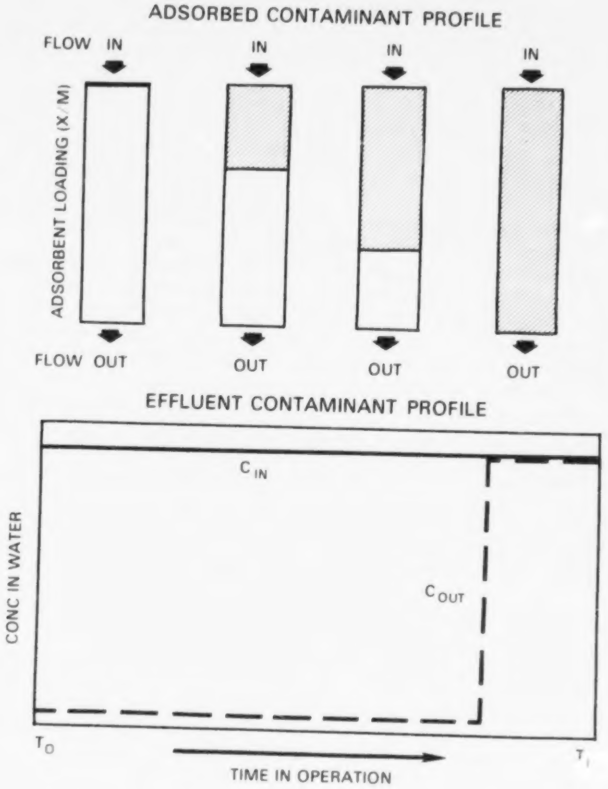

ADSORBED CONTAMINANT PROFILE
FLOW IN
IN
IN
IN
ADSORBENT LOADING (X/M)
FLOW OUT
OUT
OUT
OUT
EFFLUENT CONTAMINANT PROFILE
C_{IN}
CONC IN WATER
C_{OUT}
T_O
T_I
TIME IN OPERATION

Figure 36. Ideal adsorption column performance.

TABLE 18. THEORETICAL TIME IN SERVICE UNTIL EXHAUSTION FOR TRIHALOMETHANE ADSORPTION

Constituent	Influent concentration (μg/L)	Loading at equilibrium* (mg/g)	Time to exhaustion†‡ (days)
$CHCl_3$	75	0.35	15
$CHBrCl_2$	50	1.3	87
$CHBr_2Cl$	25	1.4	189
$CHBr_3$	10	1.8	606

*From Figure 29.[51]

†10 minute EBCT, approach velocity = 5 m/hr (2 gpm/ft²), GAC density = 490 kg/m³ (30 lb/ft³).

‡Exhaustion for total trihalomethanes will not occur until the species with the best adsorption characteristic reaches exhaustion.

Because, in this example, chloroform is present in the highest concentration and is the trihalomethane most poorly adsorbed, the "service time to exhaustion" is the shortest for that compound.

This same approach can be used to estimate the influence of the three factors that control the time in service to exhaustion for a GAC adsorber. Based on the adsorption isotherm data (Figure 29), the data in Table 19 show that, to a varying degree, EBCT, influent concentration, and trihalomethane species all have an influence on the calculated time in service to exhaustion.

TABLE 19. INFLUENCE OF INFLUENT CONCENTRATION, EMPTY BED CONTACT TIME, AND SPECIES OF TRIHALOMETHANE ON SERVICE TIME TO EXHAUSTION* OF GRANULAR ACTIVATED CARBON†

Constituent/ EBCT (minutes)	Influent concentration at exhaustion ($\mu g/L$)		
	5‡	25	100
Chloroform			
3	10 days§	7 days	5 days
10	34 days	24 days	16 days
40	135 days	96 days	66 days
Bromoform			
3	242 days	117 days	61 days
10	808 days	390 days	202 days
40	3232 days	1560 days	808 days

*Based on Figure 29.[51]

†Approach velocity = 5 m/hr (2 gpm/ft²); GAC density = 490 kg/m³ (30 lb/ft³).

‡Figure 29 extrapolated to this concentration.

§Service time to exhaustion.

When the other two variables are constant, the time in service to exhaustion is directly proportional to EBCT. For chloroform, a twenty-fold increase in influent concentration resulted in a 50 percent decline in the service time to exhaustion, whereas the same increase in the bromoform influent concentration caused a 75 percent decline in the service time to exhaustion. Finally, the time in service to exhaustion for bromoform was 24, 16, and 12 times longer than that for chloroform at the influent concentrations of 5 $\mu g/L$, 25 $\mu g/L$, and 100 $\mu g/L$, respectively.

Although this approach may be useful to determine the service life of an ideal adsorber, these estimates may be of only marginal use in practice. Various parameters affecting the rate of mass transfer within the adsorber (kinetic aspects of adsorption) severely limit its application, and make necessary the use of pilot column studies for accurate prediction of performance.

Schematically illustrated in Figure 37 is a diagram showing the concentration of adsorbed species on the surface of the adsorbent (X/M) with bed depth. Under operational conditions, adsorbed material accumulates at the top of the bed until the amount adsorbed is in equilibrium with the influent contaminant concentration. At this time the adsorbent is loaded to capacity and that portion of the bed is exhausted. Below that zone is a second zone where dynamic adsorption is taking place, i.e., the contaminant is being transferred from the liquid solute to the adsorbed phase. This zone is called the "mass transfer zone,"[57] and its depth (deviation from ideal plug flow) is controlled by many factors, depending on the contaminant being adsorbed, characteristics of the adsorbent, hydraulic factors, and others. The depth of the mass transfer zone is a measure of physical/chemical resistance to mass transfer. Once formed, the mass transfer zone moves down through the adsorbent bed until it reaches the bottom, whereupon the effluent concentration of the contaminant in the

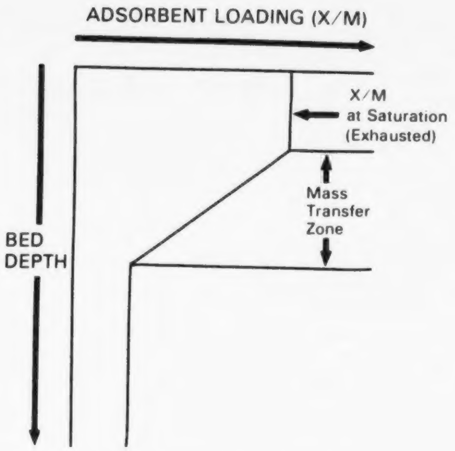


Figure 37. Mass transfer zone in a GAC adsorber.

aqueous phase begins to rise (Figure 38). Figure 38A shows the concentration gradient of adsorbed material (X/M) in an adsorber as the mass transfer zone moves down the column with time. As the mass transfer zone reaches the bottom of the column, "breakthrough" of the contaminant occurs as noted by a detectable increase in effluent concentration (Figure 38B). When the adsorber is operated to exhaustion (at equilibrium; $C_{IN} = C_{OUT}$), the breakthrough profile (plot of effluent concentration with time) takes on a classical "S" shape — a shape controlled by the shape and length of the mass transfer zone.

Thus, any estimate from isotherm data of a dynamic adsorber service time to exhaustion is at least subject to error caused by the differences in mass loading calculations based on ideal plug flow (Figure 36) and typical column performance (Figure 38) as represented by Areas A and B in the effluent concentration profile (Figure 38B). Clearly, undesirable concentrations of contaminant may appear long before exhaustion occurs in practice.

When an adsorber is removing *all* of a contaminant, the mass transfer zone in Figure 37 may also be called the "critical depth" because this is the minimum design depth for an adsorber that will allow it to remove all of a contaminant. Although the mass transfer zone is constant for a given situation (based on the contaminant, its concentration, the adsorbent used, and the flow rate), the critical depth changes depending on the allowable effluent target. This change is because the critical depth is defined as the minimum design depth for an adsorber that will allow it to achieve some target effluent concentration. The higher the target effluent concentration, the smaller the critical bed depth.

Figure 39 is a schematic illustration of the concentration profile of a contaminant in solution within an adsorber in the region of the mass transfer zone showing the relationship between the size of the critical depth and three different target effluent concentrations. In Figure 39A, the effluent target concentration is not reached because the physical bed depth is less than the critical depth. Figure 39B shows that the effluent target is reached because the bed is deeper than the critical depth, and 39C shows a decrease in critical depth for a less stringent effluent target concentration. Finally, if the adsorber can be allowed to operate to exhaustion, then the critical depth becomes zero as the target effluent concentration would equal the influent concentration.

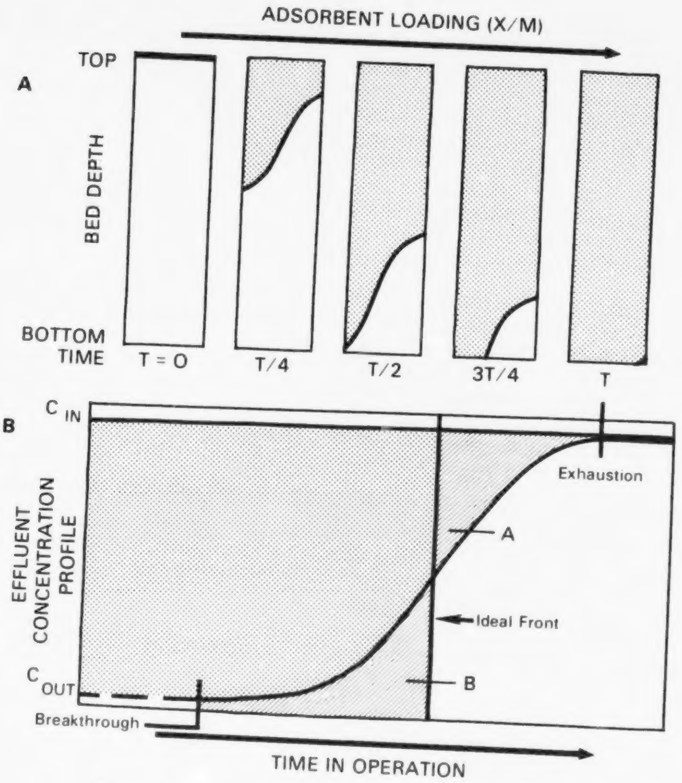
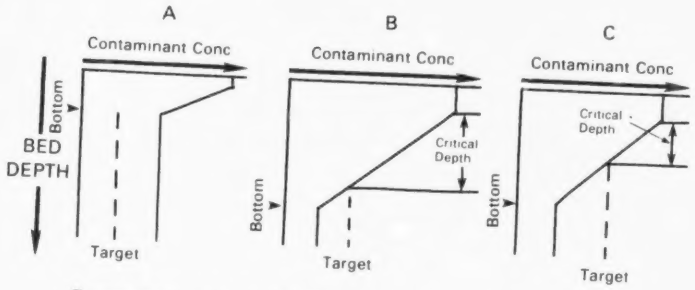

ADSORBENT LOADING (X/M)
A
TOP
BED DEPTH
BOTTOM
TIME
T = O
T/4
T/2
3T/4
T
B
C IN
EFFLUENT CONCENTRATION PROFILE
Exhaustion
A
Ideal Front
B
C OUT
Breakthrough
TIME IN OPERATION

Figure 38. Typical adsorption column performance.


A
Contaminant Conc
Bottom
BED DEPTH
Target
B
Contaminant Conc
Critical Depth
Bottom
Target
C
Contaminant Conc
Critical Depth
Bottom
Target

Target not reached, bed depth less than critical depth

Target Reached

Smaller critical Depth with Higher Target Concentration

Figure 39. Critical depth relationships in a GAC adsorber.

From the above discussion, an additional factor complicating predictions of adsorber service life can be deduced, namely, the effect of changing the influent concentration of the contaminant. For example, if after a period of time in service the influent concentration of the contaminant suddenly decreases, previously adsorbed material must desorb to establish a new equilibrium condition. This desorption creates a higher-than-predicted "wave" of contaminant concentration to move down the column. In the extreme, the effluent concentration of a given contaminant may be higher than the influent concentration for a period of time. "Chromatographic" effects caused by displacement of the adsorbed contaminant by other materials with stronger adsorption characteristics also cause desorption to occur with similar effluent/influent characteristics being observed.

Experimental Results—For the studies done in-house by USEPA's Drinking Water Research Division, glass columns, 3.7 cm (1.5 in) in diameter, filled with different depths and types of GAC (Table 20), were exposed to Cincinnati tap water at various approach velocities and empty bed contact times to determine the ability of GAC to remove chloroform and two other trihalomethanes. At an approach velocity of 5 m/hr (2 gpm/ft^2), the decrease in trihalomethane concentrations through 76 cm (30 in) of a coal base and through a lignite base GAC are shown in Figures 40 and 41, respectively. These systems each had an EBCT of 9 minutes.

TABLE 20. GRANULAR ACTIVATED CARBON CHARACTERISTICS

	Coal base Filtrasorb® 200	Coal base Filtrasorb® 400	Lignite base* HD 10x30
Surface area by nitrogen gas BET method			
m^2/g	850-900	1050-1200	600
Density			
kg/m^3	490	410	385
lb/ft^3	30	25	23.5

*Hydrodarco® 1030 manufactured by ICI America, Inc., Atlas Chemicals Division, Wilmington, DE 19899, hereafter called HD 10x30.

These columns were started at different times, but the trihalomethane breakthrough patterns are similar. The chloroform concentration was lowered 90 percent or more for about 3 weeks, then the effluent chloroform concentration steadily increased until it equalled the influent concentration at about the ninth or tenth week. The trihalomethanes containing bromine were more effectively adsorbed by the GAC. Positive reductions were observed for 26 to 30 weeks for bromodichloromethane and for about 40 weeks for dibromochloromethane (Figure 42, page 69) because of both a lower concentration in the water and because the bromine-containing trihalomethanes are better adsorbed (Table 18, Figure 29). In 1976, Rook reported similar findings.[26]

Because adsorption is a reversible process, after the bed is exhausted and if the contaminant concentration declines, a new equilibrium will be established with less material adsorbed on the adsorbent. To reach this lower adsorbent loading, desorption must occur. In this study, periods existed when the effluent trihalomethane concentrations exceeded the influent, e.g., note chloroform and bromodichloromethane desorption in Figure 42. A material balance after 30 weeks, however, accounted for all but 6 percent of the total trihalomethane influent to the coal base GAC system and 16 percent to the lignite base GAC system. The influent total trihalomethane loading used in the material balance was a summation of the product of the averaged weekly flows and the influent total trihalomethane concentrations.

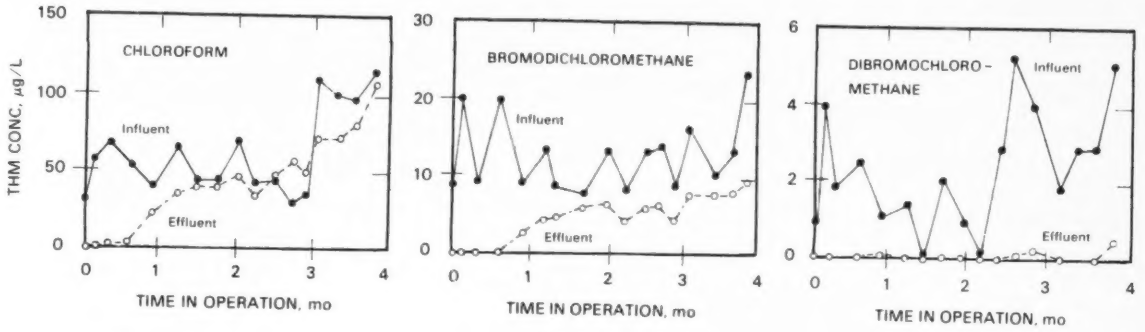


Figure 40. Removal of trihalomethanes from Cincinnati, OH, tap water by coal-base GAC. Test period, February–May 1975; GAC type, Filtrasorb® 200, bed depth, 76 cm (30 in); hydraulic loading, 5 m/hr (2 gpm/ft²), EBCT, 9 min. Bromoform was not found.

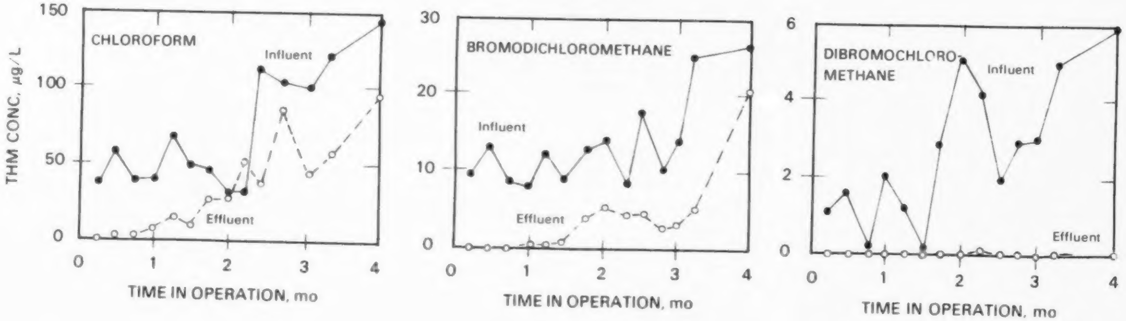


Figure 41. Removal of trihalomethanes from Cincinnati, OH, tap water by lignite-base GAC. Test period, March–June 1975; GAC type, HD 10 × 30; bed depth, 76 cm (30 in); hydraulic loading, 5 m/hr (2 gpm/ft²); EBCT, 9 min. Bromoform was not found.

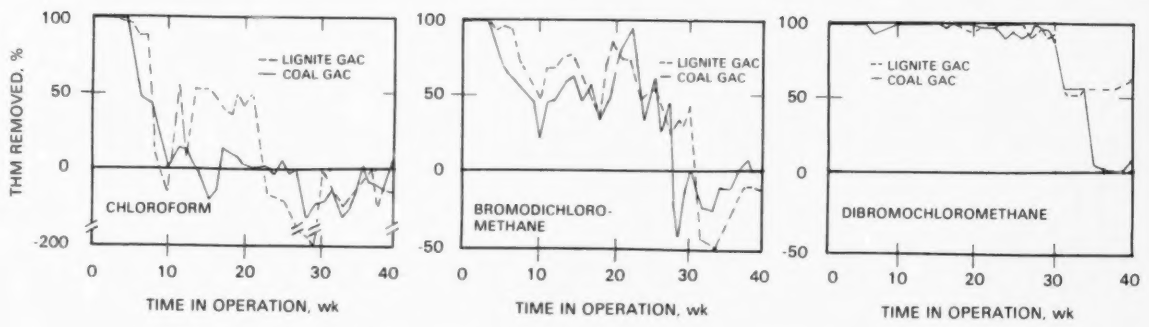


Figure 42. Comparison of removal of trihalomethanes from Cincinnati, OH, tap water using two types of GAC. GAC type: lignite base, HD 10 × 30; coal base, Filtrasorb® 200; bed depth, 76 cm (30 in); hydraulic loading, 5 m/hr (2 gpm/ft²); EBCT, 9 min. Bromoform was not found.

The trends shown in Figures 40 and 41 have been observed many times by others. For example, from the data ORSANCO collected at the Huntington Water Corporation on a full-scale GAC bed, as expected, the time to exhaustion is greater for the trihalomethanes containing bromine than for chloroform[18] (Figure 43).

A recent study at the Cincinnati, Ohio, water treatment plant compared the performance of four 10-cm (4-in) diameter pilot columns receiving chlorinated filtered water for the removal of trihalomethanes.[30] Different adsorbent depths were used to produce four different EBCT's. These data (Figure 44) show the influence of both EBCT and trihalomethane species on the removal of these contaminants by adsorption. Note, the point of chlorination was moved closer in the treatment train to the test units on 12/4/78, and the shorter reaction time resulted in lower influent trihalomethane concentrations.

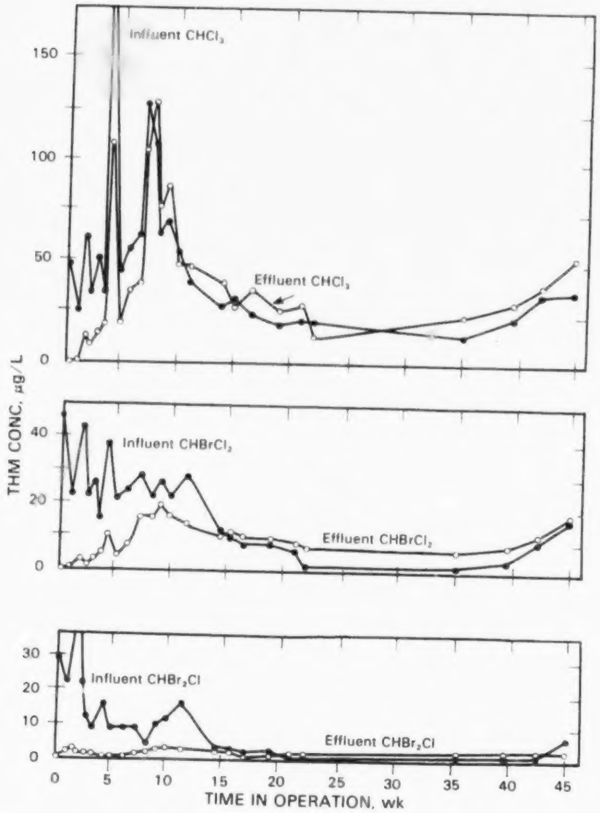


Figure 43. Trihalomethane removal at the Huntington Water Corporation by GAC. GAC type, WVW 14 × 40; bed depth, 76 cm (30 in); approach velocity, 6.1 m/hr (2.6 gpm/ft²); EBCT, 7.1 min.[18]

GAC manufactured by four U.S. companies was compared for the adsorption of chloroform at Miami, Florida.[31] In this case, four parallel 2.5-cm (1-in) diameter glass columns received filtered water from the treatment plant. These data (Figure 45, page 74) show three GAC's—the WVG,* the HD × 30, and the F-400—performed similarly, agreeing with the results of the earlier comparison of HD 10 × 30 and F-200 (Figure 42). These data also show that only the W950† GAC was significantly better than the other three materials.

Data on the adsorption of trihalomethanes on virgin GAC have been assembled (Table 21, page 75). Because the influent concentration of TTHM was less than the MCL in the Trihalomethane Regulation[1] for many of these studies, tabulating a time to reach the MCL was not possible in those cases. Therefore, as a measure of when the adsorption process stopped, the time to reach exhaustion for TTHM removal was tabulated for each location. This, then, shows the general effectiveness of GAC adsorption in a variety of places.

Because of the strong influence of EBCT on the service time to exhaustion (Table 19, Figure 44), the data have been ranked in ascending order of EBCT. The mix of trihalomethane species also influences the service time to exhaustion (Table 19). Because of this, the Cl/Br ratio in the influent trihalomethanes at the time of exhaustion is reported as a way to indicate the mixture in that particular water. Finally, because the average influent concentration of TTHM influences adsorption (Table 19), this information is also given. These data should help the reader select for further study the reference citation of most interest. Combining data from different locations cannot be done reliably, but generally (Table 21), for typical EBCT's, service time to exhaustion is quite short.

Finally, Blanck showed that at the Davenport, Iowa, water treatment plant nearly 80 percent breakthrough of TTHM occurred on or before 14 weeks of operation (Table 22, page 78).[66]

As noted earlier, if some effluent concentration less than the influent concentration, such as the MCL for TTHM, is chosen as the target performance criteria for GAC adsorber, a critical depth will be established. This then is the minimum design depth of the adsorber that will enable the target concentration to be reached. To illustrate this, the chloroform data from Table 23 (page 78)[59] are plotted in Figure 46 (page 79). Here, both the "service time to exhaustion" and the "service time to some target less than exhaustion" (arbitrarily selected as 2 μg/L for chloroform in this case) are positively correlated to bed depth or EBCT. The minimum bed depth or critical depth to remove the chloroform to the target concentration of 2 μg/L is 49 cm (1.6 ft) for these data.

Of course, the closer the target concentration is to the exhaustion (influent) concentration, the smaller is the minimum bed depth required to meet the target concentration. Further, as shown in Figure 39, when measuring service time to exhaustion, the target effluent concentration equalling the influent concentration, the critical depth is zero. The vertical distance in weeks between the two lines in Figure 46 is a measure of the error in predicting service life if equilibrium (exhaustion) studies are used, when the treatment target is not exhaustion but a lower effluent chloroform concentration (2 μg/L in this case).

Figure 47 (page 79)[59] showing the "bed depth-service time" plots[68] for the four trihalomethanes in Table 23 demonstrates that the more strongly adsorbed bromine-containing trihalomethanes have a smaller critical bed depth, that is, a thinner mass transfer zone. Waters in which the mixture of trihalomethanes is dominated by the bromine-containing species might be effectively treated longer and with shallower GAC beds than waters containing predominantly chloroform.

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*Nuchar® WV-G manufactured by Westvaco Corporation, Covington, VA 24426, hereafter called WVG. When available the Mesh size, e.g., 12 × 40, is included. Other types of GAC such as Nuchar® WV-W are WVW.

†WITCARB® Grade 950 manufactured by Witco Chemical Corporation, Inorganic Specialties Division, New York, NY 10017, hereafter called W950.

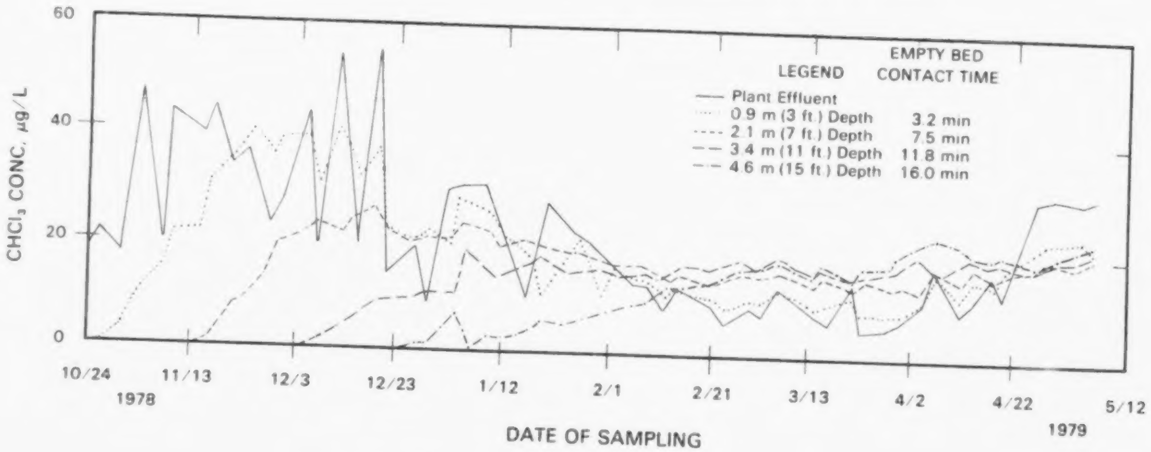

Figure 44. Removal of trihalomethanes by GAC at the Cincinnati Water Works (OH). GAC type, WVG.[30]

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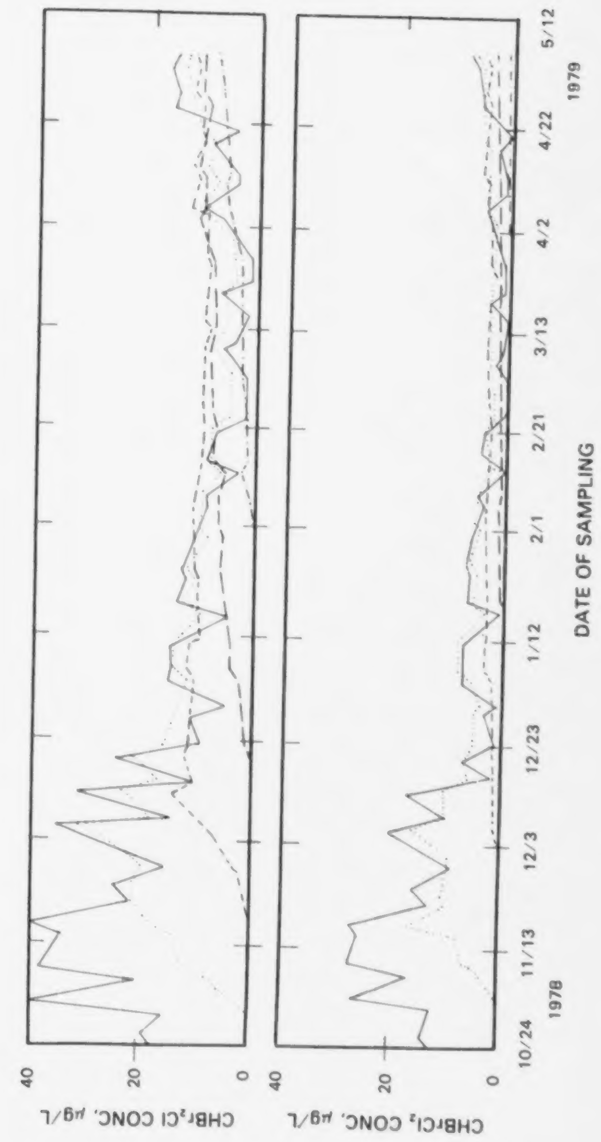

Figure 44. (Continued)

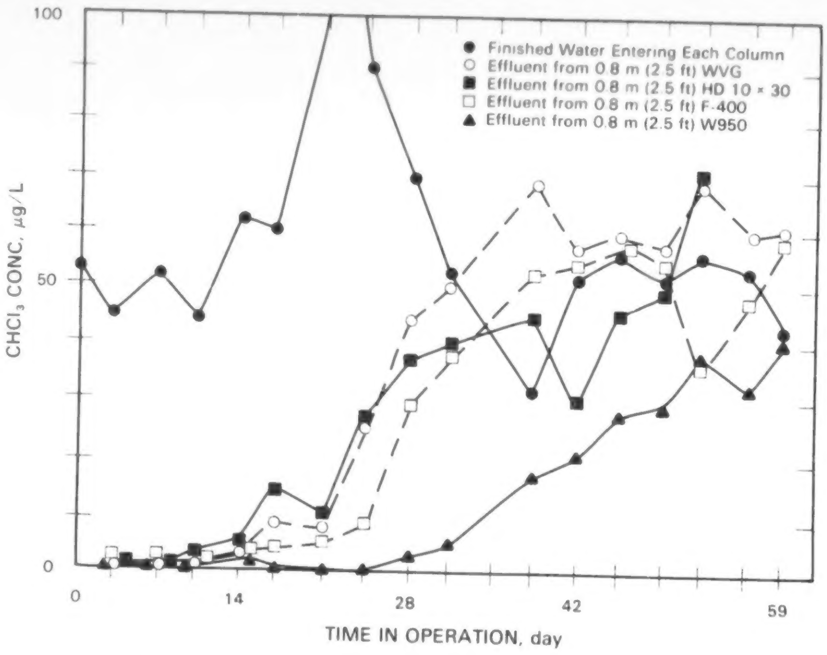

Figure 45. Chloroform breakthrough curves through four types of GAC columns at Miami, FL. EBCT, 6.2 min.[31]

TABLE 21. SUMMARY OF DATA ON ADSORPTION OF TOTAL TRIHALOMETHANES ON VIRGIN GRANULAR ACTIVATED CARBON (GAC)

Location	Type of GAC	Type of system	EBCT (minutes)	Cl/Br ratio*†	Influent TTHM Concentration† (μg/L)	Time to Exhaustion‡ (weeks)	Ref.
Cincinnati, OH	WVG 12x40	PC/PA§	3.2	2.3	50	5	30
Cincinnati, OH	HD 10x30	PC/PA	3.2	1.9	71	4	30
Cincinnati, OH	WVG 12x40	FS/SR§	4.5	2.3	51	22	62
Cincinnati, OH	Filtrasorb® 400	PC/PA	5	2.3	121	6	IH§
Mt. Clemens, MI	HD 3000**	FS/SR	5.8	4.4	22	13	NR§
Mt. Clemens, MI	HD 3000**	FS/SR	5.8	4.6	25	12	NR
Miami, FL	Filtrasorb® 400	PC/PA	6.2	1.8	156	12	59
Evansville, IN	HD 10x30	PC/PA	6.6	13.2	0.7	3	63
Huntington, WV	WVW 14x40	FS/SR	7.1	11.3	145	7	18
Cincinnati, OH	HD 10x30	PC/PA	7.5	2.9	31	8	30
Cincinnati, OH	WVG	PC/PA	7.5	3.8	31	8	30
Cincinnati, OH	WVG 20x50	FS/SR	7.5	4.1	51	22	62
Cincinnati, OH	WVG 12x40	FS/SR	7.5	2.3	51	22	62
Philadelphia, PA	UNK§	PC/PA	7.5	INF§	80	9	58
Little Falls, NJ	HD 10x30	FS/PA	8	12	91	14	65
Little Falls, NJ	WVW	FS/PA	8	52	123	13	65
Little Falls, NJ	Filtrasorb® 400	FS/PA	8	12	91	14	65
Cincinnati, OH	HD 10x30	PC/PA	9	3.0	44	9	IH
Newport, RI	Filtrasorb® 400	PC/PA	9	6.1	111	10	NR
Cincinnati, OH	Filtrasorb® 200	PC/PA	9	6.3	54	9	IH
Cincinnati, OH	WVG 12x40	PC/SR	9.4	3.4	57	22	30
Evansville, IN	HD 10x30	PC/PA	9.6	19.9	0.7	3	63
Cincinnati, OH	Filtrasorb® 400	PC/PA	10	2.3	97	12	35

Continued

TABLE 21. (Continued)

Location	Type of GAC	Type of system	EBCT (minutes)	Cl/Br ratio*†	Influent TTHM Concentration† (μg/L)	Time to Exhaustion‡ (weeks)	Ref.
Cincinnati, OH	PICA-A††	PC/PA	10	0.72	48	12	IH
Cincinnati, OH	PICA-B††	PC/PA	10	1.8	49	13	IH
Beaver Falls, PA	Filtrasorb® C‡‡	FS/SR	10.1	7.2	45	15	18
Jeff. Parish, LA	Filtrasorb® 400	PC/PA	10.9	30	3.5	8	14
Kansas City, MO	WVG	PC/PA	11	11.7	14	12	64
Kansas City, MO	HD 10x30	PC/PA	11	4.6	18	12	64
Kansas City, MO	LCK††	PC/PA	11	5.0	29	12	64
Kansas City, MO	Norit ROW††	PC/PA	11	5.5	29	12	64
Kansas City, MO	Filtrasorb® C‡‡	PC/PA	11	5.1	18	13	64
Jeff. Parish, LA	WVG	PC/PA	11.2	54.5	5.0	7	61
Beaver Falls, PA	Filtrasorb® 400	FS/SR	11.3	6.4	67	10	18
Beaver Falls, PA	HD 8x16**	FS/SR	11.4	6.4	63	9	18
Cincinnati, OH	WVG	PC/PA	11.8	4.7	8.7	16	30
Cincinnati, OH	HD 10x30	PC/PA	11.8	3.0	17	17	30
Miami, FL	Filtrasorb® 400	PC/PA	12.4	3.6	155	17	59
Jeff. Parish, LA	WVG	FS/SR	13.6	5.7	6.6	18	61
Jeff. Parish, LA	WVG	FS/SR	14	12.2	7.5	13	60
Cincinnati, OH	WVG	PC/PA	16	13.6	17	17	30
Cincinnati, OH	HD 10x30	PC/PA	16	7.9	17	17	30
Jeff. Parish, LA	WVG	PC/SR	17	10.3	5.0	16	61
Jeff. Parish, LA	WVG	FS/PA	17.5	7.3	6.4	18	61
Jeff. Parish, LA	WVG	FS/SR	18	INF	6.1	12	60
Jeff. Parish, LA	Filtrasorb® 400	FS/PA	19.3	9.0	3.3	14	14
Jeff. Parish, LA	WVG	FS/PA	20	INF	6.1	15	60

Continued

TABLE 21. (Continued)

Location	Type of GAC	Type of system	EBCT (minutes)	Cl/Br ratio*†	Influent TTHM Concentration† (μg/L)	Time to Exhaustion‡ (weeks)	Ref.
Jeff. Parish, LA	Filtrasorb® 400	PC/PA	21.4	10.0	2.4	14	14
Jeff. Parish, LA	Filtrasorb® 400	PC/SR	21.6	33.0	3.8	15	14
Jeff. Parish, LA	Filtrasorb® 400	FS/SR	21.9	10.0	2.4	14	14
Jeff. Parish, LA	WVG	PC/PA	22.1	74.8	4.3	16	61
Jeff. Parish, LA	Filtrasorb® 400	PC/PA	22.6	INF	5.5	14	14
Jeff. Parish, LA	WVG	PC/PA	25.3	9.0	4.4	18	61
Jeff. Parish, LA	WVG	FS/PA	26	20.8	4.0	>25	60
Jeff. Parish, LA	WVG	PC/PA	32.6	88.8	3.0	26	61
Jeff. Parish, LA	Filtrasorb® 400	PC/PA	34.6	INF	3.6	18	14
Jeff. Parish, LA	WVG	PC/PA	43.5	INF	UNK	>26	61
Jeff. Parish, LA	Filtrasorb® 400	PC/PA	46.3	INF	UNK	>26	14

*μg/L/μg/L.

†At time of exhaustion.

‡Service time until effluent concentration nearly equals influent concentration.

§FS, Full scale.
IH, In-house.
INF, Infinite, chloroform only present.
NR, Not reported.
PA, Post-filter adsorber.
PC, Pilot column.
SR, Sand replacement.
UNK, Unknown.

**Manufactured by ICI America Inc., Atlas Chemicals Division, Wilmington, DE 19899.

††Foreign.

‡‡Not commercially available.

TABLE 22. REMOVAL OF TRIHALOMETHANES AT DAVENPORT, IOWA, BY GRANULAR ACTIVATED CARBON (GAC)[66]

Age of GAC (weeks)	TTHM (μg/L) Influent	TTHM (μg/L) Effluent	Percent removal
14	152	120	21
18	93	97	-4
22	71	62	13

TABLE 23. REMOVAL OF TRIHALOMETHANES IN MIAMI, FLORIDA, WATER BY GRANULAR ACTIVATED CARBON[*] ADSORPTION[59]

Compound	Bed depth m	Bed depth ft	EBCT (minutes)	Average influent concentration (μg/L)	Time to 2 μg/L breakthrough (weeks)	Time to exhaustion[†] (weeks)
$CHCl_3$	0.8	2.5	6.2	67	1.1	3.4
	1.5	5.0	12	67	4.1	7.0
	2.3	7.5	19	67	7.0	10.9
	3.0	10.0	25	67	10.3	14.0[*]
$CHBrCl_2$	0.8	2.5	6.2	47	2.0	8.0
	1.5	5.0	12	47	6.0	14.0
	2.3	7.5	19	47	10.4	19.9
	3.0	10.0	25	47	15.0	CE[‡]
$CHBr_2Cl$	0.8	2.5	6.2	34	3.0	14.4
	1.5	5.0	12	34	8.4	24.8
	2.3	7.5	19	34	14.0	CE
	3.0	10.0	25	34	CE	CE
$CHBr_3$	0.8	2.5	6.2	2.5	6.0	13.4
	1.5	5.0	12	2.5	13.0	CE
	2.3	7.5	19	2.5	CE	CE
	3.0	10.0	25	2.5	CE	CE

[*] Filtrasorb® 400.

[†] Sometimes predicted by extrapolation.

[‡] Cannot extrapolate.

Finally, in a GAC adsorption bed, EBCT is influenced both by bed depth and approach velocity. Therefore, various combinations of these two factors can produce the same EBCT. Figure 48 illustrates a study where both the flow rate and GAC depth were manipulated to give a constant EBCT. These data show that, in this case, the various combinations of approach velocity and bed depth that produced a 9- or 18-minute EBCT resulted in the same chloroform breakthrough pattern. This may not be extrapolated to extremes, however. When a very shallow bed depth and a very slow approach velocity are used a reasonable EBCT might result, but because the size of the resulting critical depth may be too large under these operating conditions, a low target concentration may not be reached.

Discussion—Using equilibrium adsorption isotherms to predict service time to exhaustion, as in Table 18, is based on several assumptions. Neglecting competitive adsorption, this approach assumes that the adsorber column performance is as

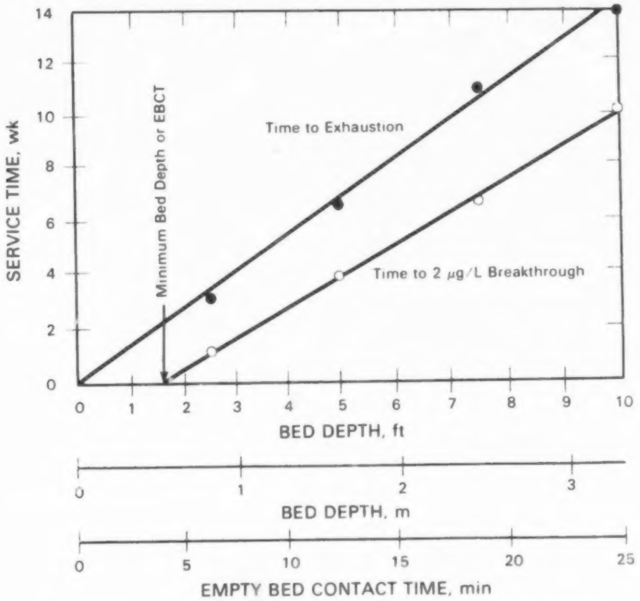

Figure 46. Bed depth-service times for the removal of chloroform in Miami, FL, water by GAC.[59]

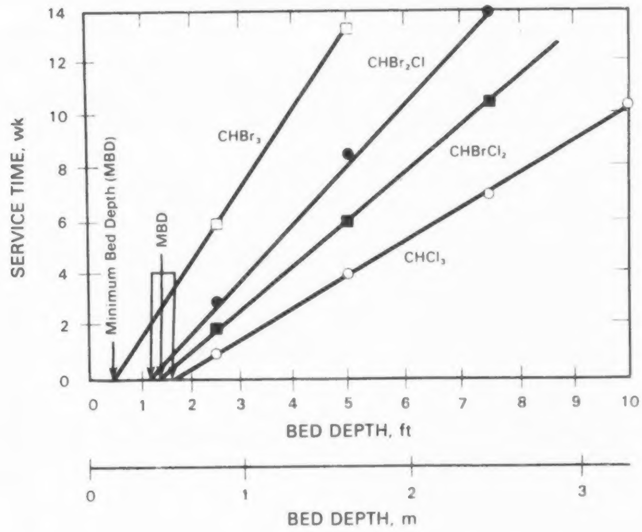

Figure 47. Bed depth-service times[68] to reach 2 μg/L in the effluent for the trihalomethanes being adsorbed by GAC.[59,67]

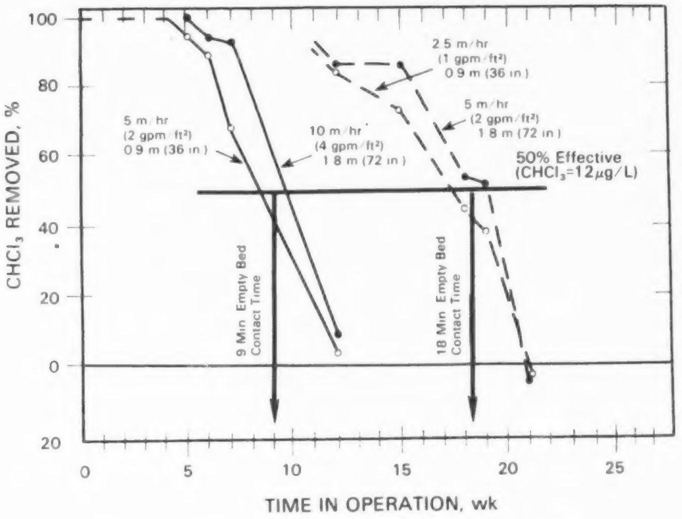

Figure 48. Effect of empty bed contact time on chloroform adsorption on GAC using Cincinnati, OH, tap water. Average applied chloroform concentration, 24 μg/L; GAC type, Filtrasorb® 400.

shown in the "ideal case" (Figure 49). In the ideal case, the shaded area represents the loading on the adsorbent at exhaustion and should equal the equilibrium loading or capacity for that influent contaminant concentration.

The "typical case" in Figure 49 is what occurs in practice. The total quantity of adsorbed contaminant is "Area A + B + C," and the predicted time in service to exhaustion using equilibrium data would be calculated such that "Area B" equals "Area A." This predicted time might be quite different from the actual exhaustion time, depending on the shape of the influent concentration and breakthrough curves.

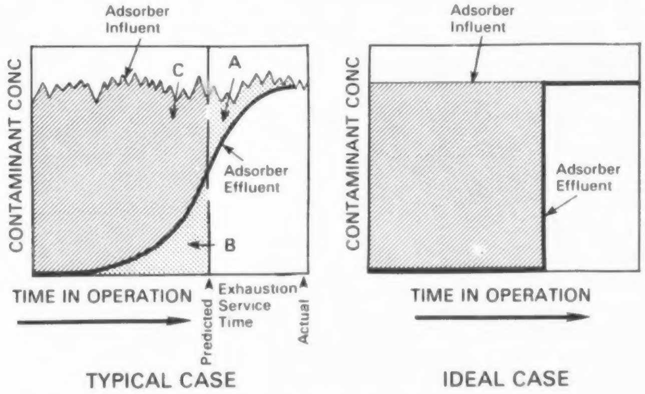
Adsorber Influent
C
A
Adsorber Effluent
B
CONTAMINANT CONC
TIME IN OPERATION
Predicted
Exhaustion Service Time
Actual
TYPICAL CASE
Adsorber Influent
Adsorber Effluent
CONTAMINANT CONC
TIME IN OPERATION
IDEAL CASE

Figure 49. Comparison of ideal and typical GAC adsorber performance.

In their work in Miami, FL, Wood and DeMarco calculated "Area A + C" to determine the GAC loading at exhaustion.[59] Although different activated carbons were used and other factors such as water quality were different, these data were compared with those determined by Dobbs and Cohen[51] (Table 24). As expected, loadings calculated from isotherm data were similar, but not the same as those observed for the GAC columns.

TABLE 24. COMPARISON OF ADSORPTION ISOTHERM DATA[51] WITH GRANULAR ACTIVATED CARBON (GAC) COLUMN ADSORPTION DATA AT EXHAUSTION[59]

Constituent	Influent concentration (μg/L)	Isotherm loading* (mg/g)	GAC column loading† (mg/g)
$CHCl_3$	67	0.35	0.67
$CHBrCl_2$	47	1.2	0.83
$CHBr_2Cl$	34	1.4	1.0

*From Figure 29[51].

†From Reference 59; bed depth = 1.5 m (5 ft); EBCT = 12 minutes.

Furthermore (referring to Figure 41), with an influent chloroform concentration of about 50 μg/L, a 9-minute EBCT, and a 5 m/hr (2 gpm/ft^2) approach velocity, use of the adsorption isotherm illustrated in Figure 28 would indicate a time in service to exhaustion of 2.6 weeks, whereas exhaustion actually occurred after 8 or 9 weeks of operation. The effects on treatment effectiveness caused by competition for adsorption sites with other organic species, as well as the difficulty in selecting the service time corresponding to "true" exhaustion when the influent concentration is highly variable, can also contribute to the disagreement between predicted and actual service times to exhaustion.

Finally, calculating service times to exhaustion from the adsorption isotherms (Figure 29) also shows that EBCT, contaminant influent concentration, and fraction of TTHM's that contain bromine all influence the service life to exhaustion (Table 19). The data in Table 21 show the influence of these three factors on the performance of GAC adsorbers.

Thus, the data in Tables 18 and 19 calculated from adsorption isotherms are instructive on a relative basis, but cannot be used to accurately predict GAC column service times. Isotherms may be used at a location to indicate the feasibility of GAC treatment, but pilot studies will always be needed to accurately predict GAC adsorber performance. The data in Table 21 also show that, generally, except for very long EBCT, service life to exhaustion is short for GAC adsorbers removing TTHM. Therefore, GAC for THM removal alone may not be recommended partly because of the high reactivation frequency required. However, if other synthetic organic contaminants are diagnosed to be a problem, then GAC might be appropriate for removing *both* these and THM's. GAC may be considered more applicable for precursor removal (especially prior to chlorination) where the required reactivation frequency may be less, to be discussed under Section VII of this report.

Synthetic Resins—

General Considerations—As alternatives to using PAC or GAC, the ability of several synthetic resins to absorb TTHM has been evaluated.

Experimental Results—Ambersorb® XE-340 *—Ambersorb® XE-340 was specifically designed to adsorb lower molecular weight halogenated organic compounds.† Cincinnati tap water containing trihalomethanes was passed through a 3.7-cm (1.5-in) diameter, glass pilot column containing 81 cm (32 in) of the resin. At an approach velocity of 5 m/hr (2 gpm/ft^2), a 10-minute EBCT resulted. The previously unpublished data in Figure 50 show that TTHM's were still being removed after 40 weeks. According to Table 21 GAC systems with a 10-minute EBCT were exhausted for TTHM removal after 12 to 15 weeks. Thus the synthetic resin appeared in this case to be significantly more effective than granular activated carbon for THM removal.

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*Ambersorb® XE-340 manufactured by Rohm & Haas Company, Philadelphia, PA 19105.

†Another advantage claimed by the manufacturer is the ability to regenerate this material in-place by steaming.

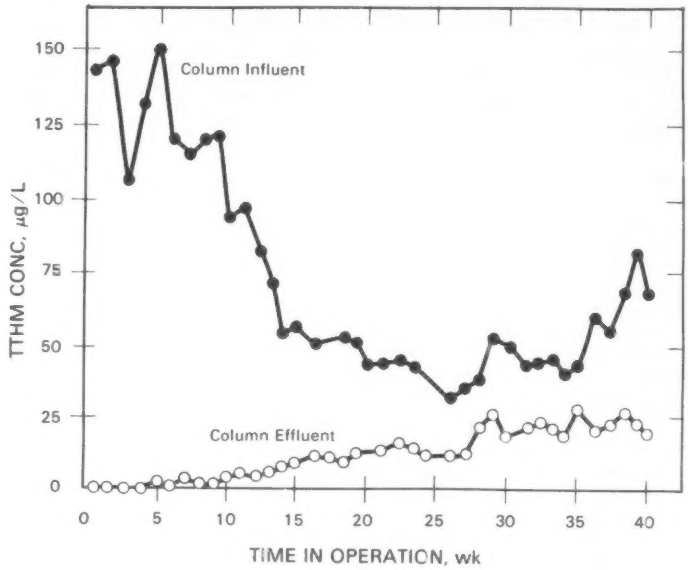

Figure 50. Removal of trihalomethanes by Ambersorb® XE-340; EBCT, 10 min.

Studies in Miami, FL, confirm the capacity of Ambersorb® XE-340 to remove trihalomethanes (Table 25).[59] As with GAC (Table 23), the time for this resin to reach exhaustion is longer for the bromine-containing trihalomethanes than for chloroform.

The comparison of trihalomethane loadings on the two adsorbents at similar influent concentrations (Table 26) shows the increased adsorption capabilities for the Ambersorb® XE-340.

Between February 1977 and March 1979, the American Water Works Association Research Foundation, along with the University of Missouri, Iowa State University, and the University of Illinois, conducted pilot scale adsorption studies at the Kansas City, Missouri, Water Treatment Plant.[64] There, Missouri River water receives coagulants, lime for softening, settling, filtration, and approximately 6 hours of free chlorine contact time before ammonia is added to ensure a combined residual. Pilot scale adsorption units (described in detail in Reference 64) were installed following filtration. They were 15-cm (6-in) diameter glass columns containing 0.9 m to 2.7 m (3 ft to 9 ft) of adsorbent. Over a 2-year period, Ambersorb® XE-340 was examined for its effectiveness for removing trihalomethanes. Variations in the trihalomethane concentrations in the applied water makes selecting an absolute time for breakthrough (effluent >10 percent of influent) and exhaustion difficult; however, Ambersorb® XE-340 effectively removed trihalomethanes, exhibited a very gradual

TABLE 25. REMOVAL OF TRIHALOMETHANES IN MIAMI, FLORIDA, BY SYNTHETIC RESIN*[59]

Compound	Average influent concentration (μg/L)	Time to 2 μg/L breakthrough (weeks)	Time to exhaustion† (weeks)
$CHCl_3$	80	3	156
	69	3	150
	64	0	150
$CHBrCl_2$	37	20	216
	43	20	210
	42	22	CE‡
$CHBr_2Cl$	12	47	260
	25	45	260
	27	25	CE
$CHBr_3$	1.9	63	CE

*Ambersorb® XE-340; EBCT = 6.2 minutes; bed depth = 0.8 m (2.5 ft).
†Sometimes predicted by extrapolation.
‡Cannot extrapolate.

TABLE 26. COMPARISON OF GRANULAR ACTIVATED CARBON (GAC) (F-400) AND AMBERSORB® XE-340 COLUMN DATA AT EXHAUSTION*[59]

Constituent	Influent† concentration (μg/L)	GAC column loading (mg/g)	Influent concentration (μg/L)	Ambersorb® XE-340 column loading (mg/g)
$CHCl_3$	67	0.53	69	2.2
$CHBrCl_2$	47	0.84	43	2.0
$CHBr_2Cl$	34	1.0	25	1.6

*EBCT = 6.2 minutes; bed depth = 0.8 m (2.5 ft).
†See Table 23.

breakthrough curve, and, thereby, yielded a long service life. Although effective, like any adsorbent that is not used on a one-time basis, Ambersorb® XE-340 must be regenerated when saturated with adsorbate. Also, adsorption of trihalomethanes on Ambersorb® XE-340 is a reversible process, and these materials will desorb if the influent concentration declines. This is shown in Figure 51 where chloroform-free water was passed over a bed of Ambersorb® XE-340 that had previously been exhausted for chloroform removal. Under these circumstances, the expected desorption occurred.[59]

Other Resins – Although the trihalomethanes are neutral species, strong and weak base anion exchange resins were investigated to determine their capacities to remove trihalomethanes as a part of other investigations. The strong base anion exchange resin Amberlite® IRA-904, manufactured by the Rohm & Haas Company, Philadelphia, PA 19105, was studied at both Miami, FL,[59] and Kansas City, MO;[64] the weak base anion exchange resin ES-561, manufactured by the Diamond

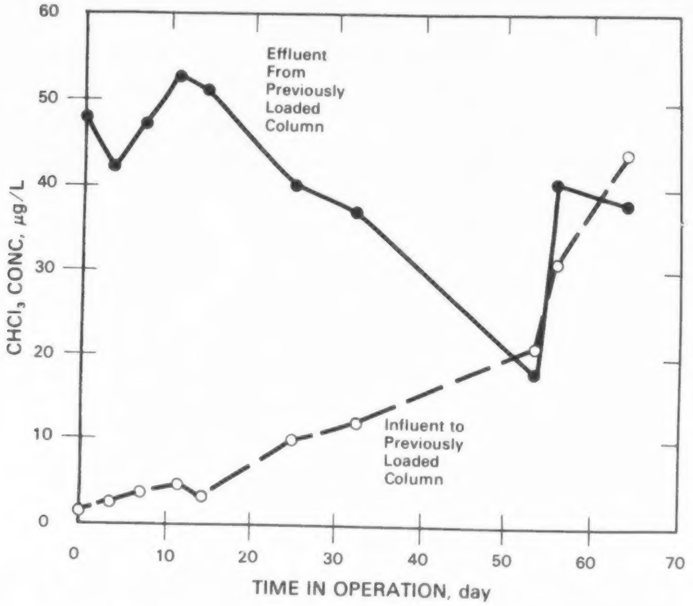

Figure 51. Desorption of chloroform from Ambersorb® XE-340; EBCT, 6.2 min.[59]

Shamrock Corporation, 800 Chester Street, Redwood City, CA 94064, was tested at Kansas City, MO.[64] As expected, these resins were not useful for removing trihalomethanes.

Discussion—Of the synthetic resins tested only Ambersorb® XE-340, the one specifically designed by the manufacturer to have high adsorptive capacity for low molecular weight halogenated compounds, showed promise. In parallel experiments loadings on this resin were greater than those on GAC. Although this resin has been regenerated by steaming in the laboratory, as claimed by the manufacturer, the scaleup to full plant size is still being developed, and this resin is not available in commercial quantities.

Summary of Using Trihalomethane Removal as an Approach to Trihalomethane Control

Advantages of Trihalomethane Removal—

As a treatment approach, removal of trihalomethanes has some advantages. The more important are that the water utility would not need to change its disinfection practices and the treatment is targeted to the regulated contaminant. Chlorination, a process in which many designers and operators have confidence, could continue to be used as a disinfection process, with the resulting trihalomethanes being removed by some unit process added to the treatment train. The flexibility to permit noncentral treatment of the finished water may also prove to be advantageous.

Disadvantages of Trihalomethane Removal—

Other Organic Disinfection Byproducts—To evaluate one disadvantage of maintaining chlorination practice and treating the trihalomethanes formed, the behavior of the other disinfection byproducts formed during disinfection with free chlorine must be understood. Recall that the reaction of free chlorine and precursors is:

FREE CHLORINE + PRECURSORS (HUMIC SUBSTANCES) AND BROMIDE → TRIHALOMETHANES + OTHER HALOGENATED AND NONHALOGENATED OXIDIZED BYPRODUCTS

As indicated by this reaction, during free chlorination, other halogenated byproducts result. Most of these byproducts cannot be measured individually by gas chromatographic techniques, but they can be estimated as a group, as "organic halogen" (OX). Although not perfect, this test[70] is useful for evaluating the behavior of nontrihalomethane halogenated byproducts during any proposed treatment scheme. Although the health significance of these halogenated byproducts has not been fully evaluated,[71] these byproducts should be viewed with suspicion. (The nature of these other chlorination byproducts is discussed in the subsection on Disinfection Byproducts in Section VIII.)

Therefore, one disadvantage of a treatment approach, the objective of which is to remove trihalomethanes after formation, is that other disinfection byproducts may not be removed by the treatment process. Although the concentration of these compounds is not now subject to regulation, minimizing their concentration, where possible, would be prudent.

Further, because chlorine is an oxidant, the possibility of producing *oxidation* byproducts during chlorination also exists (note the reaction above). At the present time, few of these oxidation byproducts can be measured, but their toxicologic significance is being evaluated.[71]

Lack of Precursor Removal—As mentioned earlier in this report, because the formation of trihalomethanes is not instantaneous, their concentrations increase in the water as it flows to the consumer. This is the second disadvantage of a treatment strategy based on the removal of trihalomethanes only. The precursor remaining in the water will react with any free chlorine present and more trihalomethanes will form after the trihalomethane treatment step.

For example, during an aeration study (see Table 9), chloroform was removed at higher air-to-water ratios, but the chloroform formation potential was not (Figure 52). The chloroform concentration did decline during aeration, but because of the lack of precursor removal, the chloroform concentration reaching the consumer would be higher than that measured in the effluent of the treatment unit process. Some benefit would be gained, however, as InstTHM concentrations would be lower at any point in the distribution system after aeration treatment than it would be before treatment. The adsorptive treatment techniques covered in this section also have an incidental precursor removal function that is more completely explained in Section VII. Avoiding post-treatment trihalomethane formation by converting all precursors into trihalomethanes before aeration is not practical because of the chlorination byproducts that would be formed and probably not removed during aeration and because of the typically slow trihalomethane formation rate.

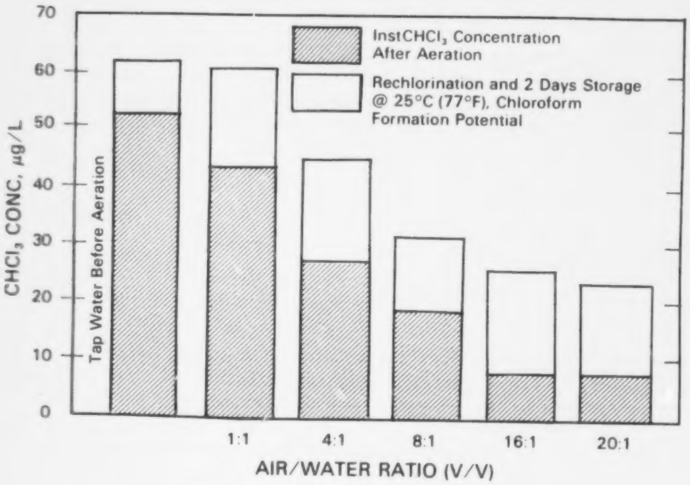

Figure 52. Removal of chloroform from Cincinnati, OH, tap water by aeration.

SECTION VII
TREATMENT TECHNIQUES TO REMOVE TRIHALOMETHANE PRECURSORS (THMFP)

Because trihalomethanes are formed when free chlorine is added to water containing trihalomethane precursors, one approach to lowering TTHM concentrations would be removal of the precursors. This section examines this approach in detail by discussing eight techniques for removing trihalomethane precursors from drinking water—clarification, source control, aeration, oxidation, adsorption, ion exchange, biologic degradation, and lowering of pH.

Trihalomethane precursors are measured by the trihalomethanes that are formed upon chlorination and storage. But the resulting measurements may be influenced greatly by variations in test conditions (storage time, temperature, pH, and trihalomethane species measured) among the locations reporting data. Thus the results presented in this section will be influenced by the varying test conditions in an unknown way. For example, two locations with the same type and quantity of precursor could report different THMFP's if the TermTHM tests were performed under different conditions.

In addition, in many experimental plant evaluations reported here, the conditions of the TermTHM test were selected and known to be somewhat different from those existing in that utility's distribution system. Thus in these cases, the TermTHM concentrations reported should not be considered to reflect actual concentrations of trihalomethanes reaching the consumer. Because of these test variables, precursor test conditions and rationales for their selection will be stated wherever possible to facilitate comparisons of data.

As discussed earlier in the "Measurement" Section, another consideration is selecting units of expression of trihalomethane concentration. This is an especially important consideration when the investigator is interpreting precursor removal data. Although, for a given amount of precursor present, observed molar yields of trihalomethanes after bromination are generally higher than when chlorination alone is practiced, this result is likely to be a reaction rate phenomenon, and the actual number of potential reactive sites (chemical equivalents) available is probably similar regardless of the attacking halogen species. So because trihalomethane precursors are measured by chlorinating a sample and analyzing the trihalomethanes produced, any summation should theoretically be made on a molar basis. Such a summation would allow the most accurate comparison of precursor concentrations (number of active sites) in various samples tested, because this measure is unbiased by the differing molecular weights of the trihalomethanes formed in varying mixtures.

Again, however, because the Trihalomethane Regulation[3] is based on TTHM summed on a weight basis ($\mu g/L$),the data will usually be reported in terms of $\mu g/L$ THMFP rather than (or in addition to) the more chemically meaningful $\mu mol/L$. Major exceptions to this are the Subsections Powdered Activated Carbon and Granular Activated Carbon (General Considerations), where adsorption isotherms of TTHM's are discussed on a micromolar basis only. These exceptions were considered necessary because of the variable relative yields of the trihalomethane species observed when different amounts of precursor were chlorinated under the same test conditions. The differing molecular weights of these species would influence the shape of THMFP adsorption isotherm curves if the summations were made on a $\mu g/L$ basis. The units reported in the cited literature vary, and reference should be made to the respective sources for data when individual species or TTHM data expressed in molar units are desired and not included here.

Clarification (Including Moving the Point of Chlorine Application)

General Considerations—

The American Water Works Association Research Committee on Coagulation has provided an excellent summary of the general subject of organics removal by coagulation.[72] The Committee recognized that although coagulation is most often considered a treatment technique for turbidity reduction, the process plays a very significant role in organics removal at the same time. This role occurs both because some organic materials are probably adsorbed on suspended particles (turbidity) and because direct interactions of the natural humic materials (usually recognized as color) take place with the coagulants themselves. Several reports have documented the stoichiometric relationship between the precipitated humic materials and coagulants.[73,74,75] The Committee report[72] concludes that both iron salts and alum are effective for removing humic and fulvic acids from water, and that cationic polymers that interact with the anionic humates can also play a useful role as coagulants for organics removal. Doses required depend on both the amount of humic material present and the pH. The pH affects both the precipitation of the coagulant and the stoichiometry of the coagulant-humate interaction by way of protonation of the humate itself. Removal of organics by coagulation is best under slightly acidic conditions, pH 4 to 6.

Iron or aluminum salts, calcium hydroxide (if softening is also a goal), and polymers are commonly used coagulants in different types of water treatment plants designed to remove color and turbidity. Thus the study of these coagulants for the removal of trihalomethane precursors was logical because a major fraction of trihalomethane precursors are humic and fulvic acids that cause natural color.

Early Experiments with Clarification Processes for Precursor Removal—Early in the USEPA in-house studies, samples were collected before and after the various unit processes within a conventionally operated pilot plant and analyzed for nonpurgeable organic carbon (NPOC) concentrations. Although removals vary, the relative results (Figure 53) are fairly typical and generally as expected, because similar results have been reported in the NORS[7] and subsequently demonstrated in another full-scale water treatment plant.[76] In these studies, coagulation, flocculation, and sedimentation had a marked effect on the general NPOC concentration—approximately a 60 percent reduction. Kavanaugh[77] also cited similar data from other literature.

To determine whether or not trihalomethane precursors were removed in a similar manner during conventional treatment, samples of source water, coagulated and settled water, and dual-media-filtered water from the USEPA pilot plant were chlorinated in closed containers to determine the production pattern of trihalomethanes (Figure 54A). These experiments revealed that the pattern for lowering the chloroform formation potential paralleled the general decline of NPOC for the various qualities of water (Figure 54B). This conventional treatment, however, had relatively much less effect on preventing the formation of bromine-containing trihalomethanes (Figure 54B). The reason is probably that bromide is not significantly affected by coagulation and remains available for oxidation to the active bromine species, which then effectively competes with chlorine in the trihalomethane formation reaction with the precursor that remains after clarification.

Work by Semmens[78] and Babcock and Singer[79] on coagulation also revealed important information about the potential of this process for removing trihalomethane precursors. Semmens showed that up to 65 percent precursor

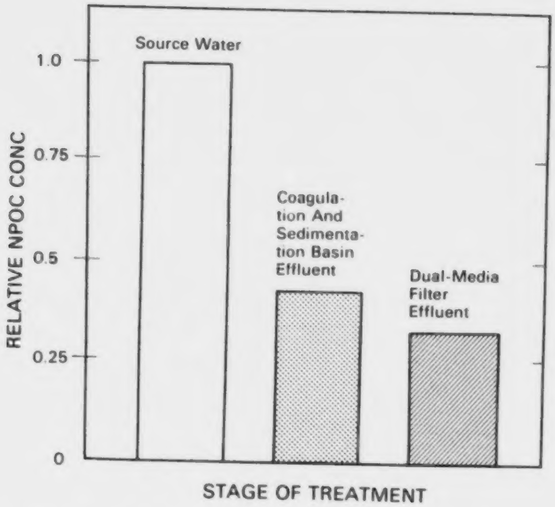

Figure 53. Relative NPOC removal during water treatment in a pilot plant. Source water NPOC concentration range, 2.2–3.9 mg/L.

removal occurred for a dose of 100 mg/L alum in reconstituted Mississippi River water at a pH range of 5.0 to 5.5. The removal of trihalomethane precursors followed the same trend as TOC and ultra-violet absorbance removal, but the relative slopes of the various removal curves were somewhat different.

Babcock and Singer[79] showed that about 80 to 90 percent of humic acid, and approximately 20 to 39 percent of fulvic acid (both with a starting concentration of 10 mg/L TOC) could be removed by the addition of 100 mg/L alum at pH 5.0. In a second series of tests, they found that a residual of 1.4 mg/L humic acid TOC (starting with 10 mg/L humic acid and 50 mg/L alum) was capable of producing about 100 μg/L of chloroform within a 48-hour chlorination time. Furthermore, they found that a residual of 7.8 mg/L fulvic acid TOC (starting with 10 mg/L fulvic acid TOC and 100 mg/L alum) was also capable of producing approximately 100 μg/L chloroform during a 48-hour chlorination time. Thus the yield of trihalomethanes from residual TOC may vary significantly, indicating that the success of coagulation for precursor removal is likely to be highly variable. Both of these investigators showed that the potential for removing trihalomethane precursors by coagulation and settling may be enhanced by carrying out this process at a lower pH.

Anticipating Success of Clarification for Precursor Removal—Successful trihalomethane control can be measured in two ways: 1) by a low finished water TermTHM (precursor) concentration, which affects the trihalomethanes formed during distribution, and 2) by a low finished water InstTHM concentration, which will benefit consumers to a varying degree, depending on their distance from the plant. Either of these results from a unit process will benefit the consumer.

At existing plants already employing clarification unit process(es), only a laboratory analysis is needed to measure TermTHM reductions through the unit processes ("Amount B" and "Amount B'" in Figure 55, page 92). The magnitude of these reductions is often quite significant. Efforts can then be made to improve plant performance for increasing the removal of precursor by modification of pH, coagulant dose, or changing the coagulant used.

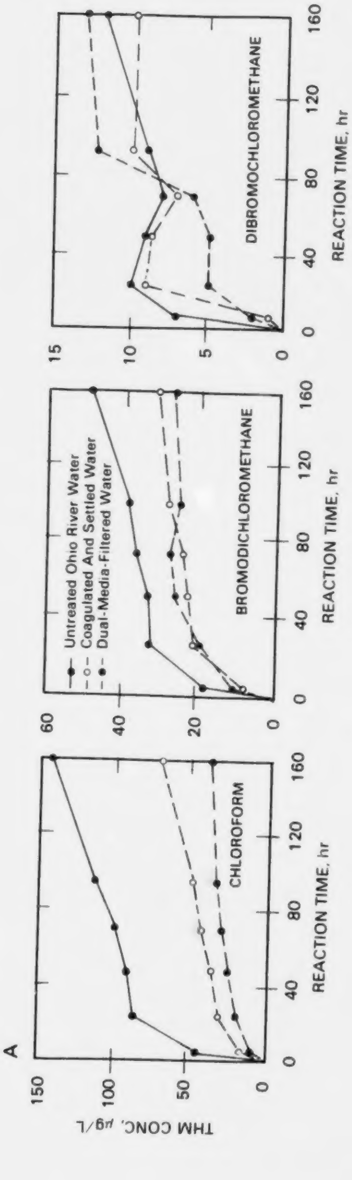

Figure 54. THMFP and NPOC in various qualities of water.

A. Production of trihalomethanes in chlorinated water samples of various qualities. Storage conditions: pH 7.4; 25°C (77°F); 5 mg/L chlorine dose.

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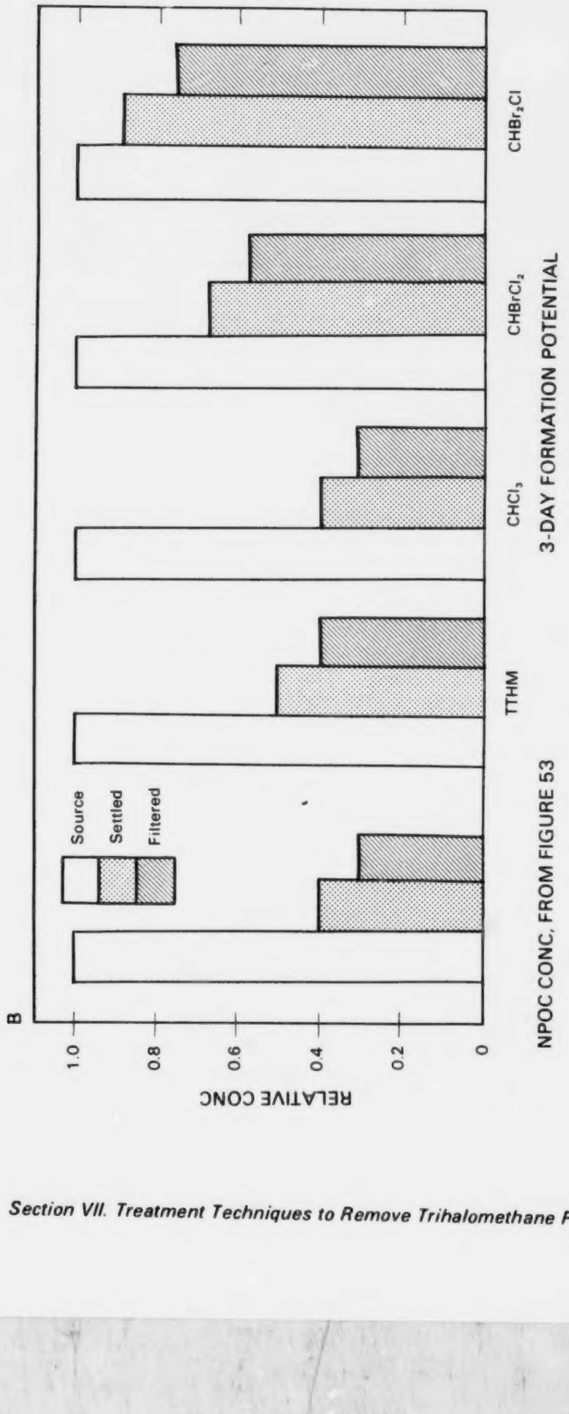


Figure 54. (Continued)

B. Comparison of THMFP and NPOC in chlorinated water samples of various qualities.

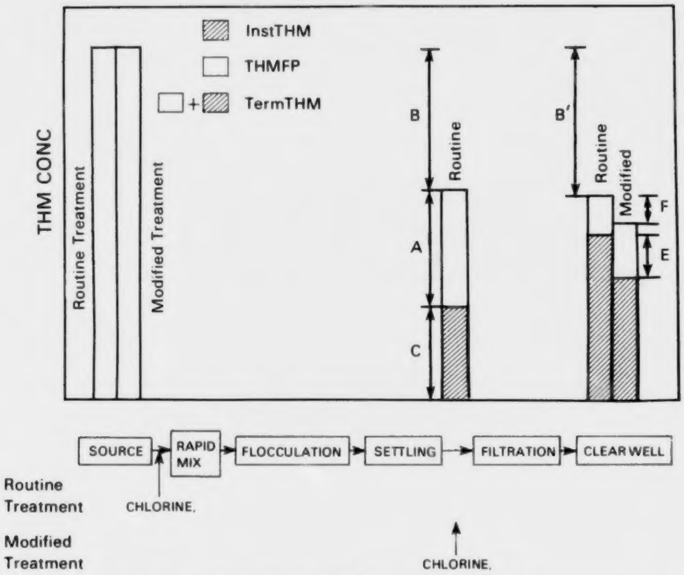


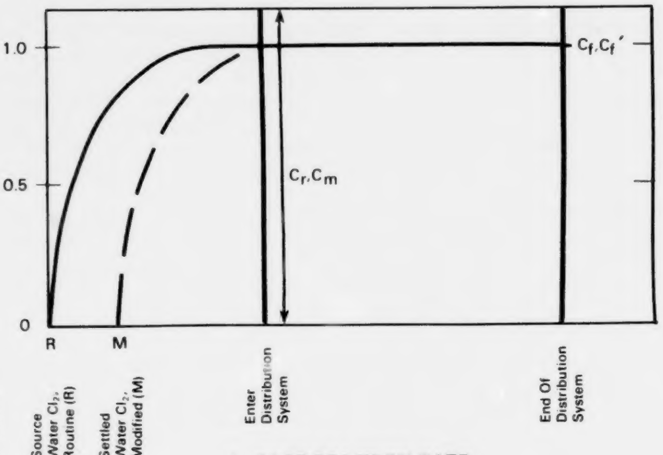
Figure 55. InstTHM, TermTHM, and THMFP relationships in conventional treatment.

Furthermore, under some circumstances, "Amount B′" can be increased by "Amount F" to reduce the finished water TermTHM concentration by moving chlorination to a point after the precipitation process is complete (see modified treatment, Figure 55). Because coagulation and settling take a significant amount of time (as opposed to most unit processes) some formation of trihalomethanes from precursors can take place during this time. This formation would be prevented if the chlorination point were moved so that additional precursor ("Amount F") could be settled before contact with the chlorine. This change in treatment practice may also decrease the finished water InstTHM concentration by "Amount E" and thereby reduce InstTHM at any given time in the distribution system.

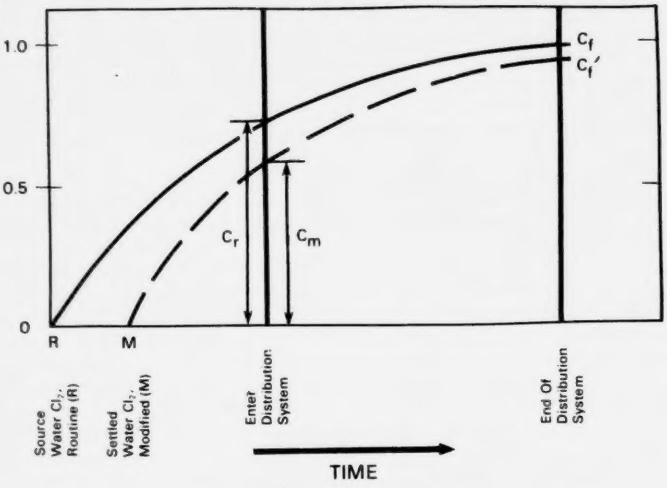
To successfully lower the finished water TermTHM concentration when the point of chlorination is moved beyond the settling basin, both the fractions $B/(A + B + C)$ and $C/(C + A)$ (Figure 55) must be high. These fractions will be reported, where available, in the Subsection on Experimental Results below to show just how high they must be.

To use this predictive technique, the fraction $B/(A + B + C)$ must be determined across the unit process after which chlorination is being considered during modified treatment, and the fraction $C/(C + A)$ must be determined on the effluent of that unit process. Furthermore, if some InstTHM is present at the point from which chlorination might be moved, this concentration must be subtracted from the measured InstTHM concentrations in the unit process effluent before calculating the fractions $C/(C + A)$ and $B/(A + B + C)$.

To successfully lower the finished water InstTHM concentration, the free chlorine/ precursor reaction must be rapid enough to be significant through the unit process, but not so rapid that the reaction is complete before the water enters the distribution system (i.e., the small reduction in contact time between the free chlorine and precursors that occurs before the clearwell when the chlorine is applied later in the treatment train must have some favorable effect in the distribution system). Figure 56 is presented to clarify this point.



A. FAST REACTION RATE.



B. TYPICAL REACTION RATE.

Figure 56. Trihalomethane concentrations resulting from delayed chlorination.

C_f = Concentration of InstTHM at end of distribution system under routine conditions.

C_f' = Concentration of InstTHM at end of distribution system under modified conditions.

C_r = Concentration of InstTHM entering distribution system under routine conditions.

C_m = Concentration of InstTHM entering distribution system under modified conditions.

For example, when conditions involve a fast reaction rate (Figure 56A), the formation of trihalomethanes is delayed when the point of chlorination is moved from R to M (routine to modified); but no difference in trihalomethane concentrations occurs at any point in the distribution system. The concentrations C_r and C_m are equal, and so are C_f and C_f'. Under the more typical reaction conditions in Figure 56B, some improvement can be noticed ($C_r - C_m$) at the entrance to the distribution system. The magnitude of this benefit decreases with time to a minimum ($C_f - C_f'$) at the end of the distribution system.

In the presentation of data from operating water treatment plants that follows, the absolute effectiveness of clarification for precursor removal, $B'/(A+B+C)$, as well as various unit process changes (including moving the point of chlorination) will be discussed together, as they are so closely related.

Experimental Results—

Coagulation-Sedimentation-Filtration—Ohio River Valley Water Sanitation Commission (ORSANCO) Results—Field studies conducted by ORSANCO measured the removal of precursor at 10 water utilities treating river water with various combinations of coagulation, settling, and filtration.[18] In this study, samples collected for determination of TermTHM were buffered to the finished water pH, received an additional 15 mg/L chlorine, and were stored for 7 days at ambient temperature. Unpublished rate curves suggested that these conditions were sufficient to complete the trihalomethane reaction so that changes in precursor concentration through a treatment process could be assessed. The curves also suggested, however, that these conditions would produce a finished water TermTHM concentration higher than would be found at the extremities of a 3-day distribution system maintaining a minimal free chlorine residual—the ambient conditions at many of these utilities. Therefore, the TermTHM concentrations do not reflect the actual quality of the consumer's drinking water even though the removal comparisons were possible.

The effectiveness of clarification as a process for trihalomethane precursor removal is demonstrated by data for the 10 locations (Table 27), which show that an average of 29 to 51 percent of the Ohio River source water precursor was removed by the treatment plants.

Three utilities—the Cincinnati Water Works, the Pittsburgh Department of Water, and the Wheeling Water Department—were selected for more detailed investigations. Two-week studies were made of trihalomethane precursor removal by individual unit processes in the treatment plant and of the effects of moving the chlorine application point further into the treatment process to allow clarification to reduce precursor concentrations before chlorination. An attempt was made to follow the InstTHM and TermTHM concentrations in a plug of water from the source through the clearwell, but not into the distribution system.

In each of these three locations, the removal of trihalomethane precursor occurred during the first unit process where a coagulant was added (Table 28, page 97). Little, if any, further removal occurred in the remaining unit processes in the treatment plant.

The Cincinnati, OH, results of moving the point of chlorination to later in the treatment train (Figure 57, page 97) show that a significant difference in source water precursor levels was observed between the two treatment periods (routine and modified, or delayed chlorination). At least a 39-percent decrease in TTHM's was noted for the source water during modified treatment. In this study, the fraction $B/(A+B+C)$ (Figure 55) during routine operation was at least 0.34, and the fraction $C/(C+A)$ was 0.26 in the settled water (Figure 57). These data show that a slightly higher percentage of the source water TermTHM concentration w[illegible]esent in the finished water during the modified mode of treatment, indicating that moving the point of chlorination from the off-stream reservoir effluent to the settling basin

TABLE 27. SUMMARY OF PRECURSOR REMOVAL DATA AT FULL-SCALE TREATMENT PLANTS[18]

Location	Treatment	Mean* fraction of precursor removal $B'/(A + B + C)$† during routine treatment	Number of tests
Huntington, WV	Coagulation, sedimentation, 2- to 3-yr-old GAC	0.29	10
Fox Chapel, PA	Coagulation, 2-stage sedimentation, filtration	0.49	12
Wilkinsburg-Pennsylvania Joint Water Authority, PA	Coagulation, 2-stage sedimentation, filtration	0.38	10
Evansville, IN	Coagulation, sedimentation, filtration	0.36	11
Pittsburgh, PA	Coagulation, 2-stage sedimentation, filtration	0.38	11
Western Pennsylvania Water Co., Hays Mine Plant	Coagulation, 2-stage sedimentation, 2- to 3-yr-old GAC	0.35	8
Beaver Falls, PA	Coagulation, 2-stage sedimentation, filtration	0.33	10
Wheeling, WV	Gravity sedimentation, coagulation, sedimentation, filtration	0.30	8

Continued

TABLE 27. (Continued)

Location	Treatment	Mean* fraction of precursor removal $B'/(A + B + C)$† during routine treatment	Number of tests
Cincinnati, OH	48-hr reservoir settling w/alum, coagulation, sedimentation, filtration	0.51	10
Louisville, KY	22-hr reservoir settling, coagulation, 2-stage sedimentation, filtration	0.28	11

*Monthly raw and finished samples.

†From Figure 55. Storage conditions: Buffer to finished water pH, 15 mg/L chlorine added, 7-day storage.

TABLE 28. SUMMARY OF PRECURSOR REMOVAL THROUGH THREE WATER TREATMENT PLANTS[18]

Location	Treatment	Mean* % removal of TermTHM† from source to effluent of given treatment
Cincinnati, OH	48-hr reservoir settling with alum	32
	Coagulation, settling	43‡
	Sand filtration	30
Pittsburgh, PA	Coagulation, clarification	29
	Settling	19‡
	Sand filtration	27
Wheeling, WV	1-hr gravity settling	0
	Coagulation, settling	18
	Sand filtration	18

*Two-week study.

†Buffer to finished water pH, 15 mg/L chlorine added, 7-day storage, ambient temperature.

‡May have been influenced by analytic error.

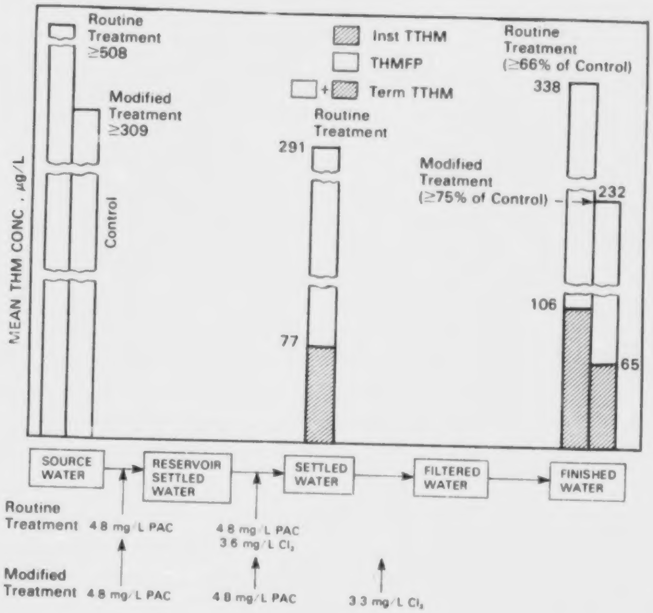


Figure 57. Trihalomethane formation (mean values) during routine and modified (delayed chlorination) treatment at the Cincinnati Water Works (OH). (October 1977, 560,000-m^3/day [150-mgd] capacity.) THMFP conditions: pH 8.4; 19 to 25°C (66 to 77°F); storage time, 7 days.[18]

effluent had little influence. On the other hand, the finished water InstTHM concentration declined 41 μg/L (39 percent), partly because the lower concentration of precursor at the time of the experiment was slowing the reaction rate. This decline benefited consumers near the water treatment plant, but additional precursor removal did not occur.

In the Pittsburgh, PA, study, the fraction B/(A + B + C) (Figure 55) during routine operation was 0.26, and the fraction C/(C + A) was 0.05 in the coagulated/clarified effluent (Figure 58). The data in Figure 58 show that the finished water TermTHM concentration did not decline, but actually rose about 2 percent during the test period. The InstTHM concentration in the finished water declined 30 μg/L (54 percent), however—a benefit to nearby consumers. The benefit of additional precursor removal did not occur as a result of changing the chlorination point. Note that in this study, the source water TermTHM concentration declined very little (about 6 percent) during the period of modified operation in contrast to the Cincinnati, OH, results reported above. So in this case, the decline in InstTHM concentration cannot be attributed to a lower source water precursor concentration.

The Wheeling, WV, study used the same technique as described above. During routine operation, the fraction of TermTHM that was removed in the coagulation/settling basin was 0.18, and the fraction of THMFP that was converted to InstTHM during that unit process was 0.23 (Figure 59). During modified

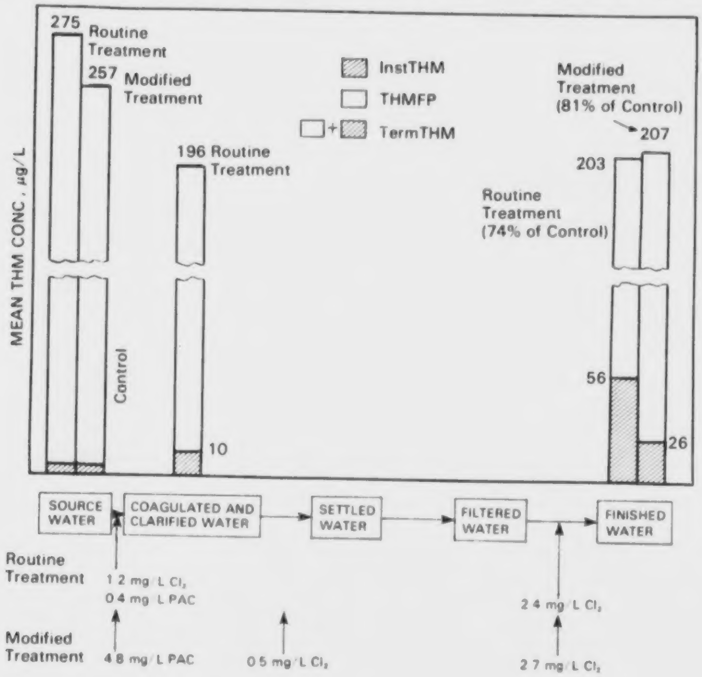


Figure 58. Trihalomethane formation (mean values) during routine and modified (delayed chlorination) treatment at the Pittsburgh Department of Water (PA). (October 1978, 228,000-m^3/d [60-mgd] capacity.) THMFP conditions: pH 8.3; 17 to 23°C (63 to 73°F); storage time, 7 days.[18]

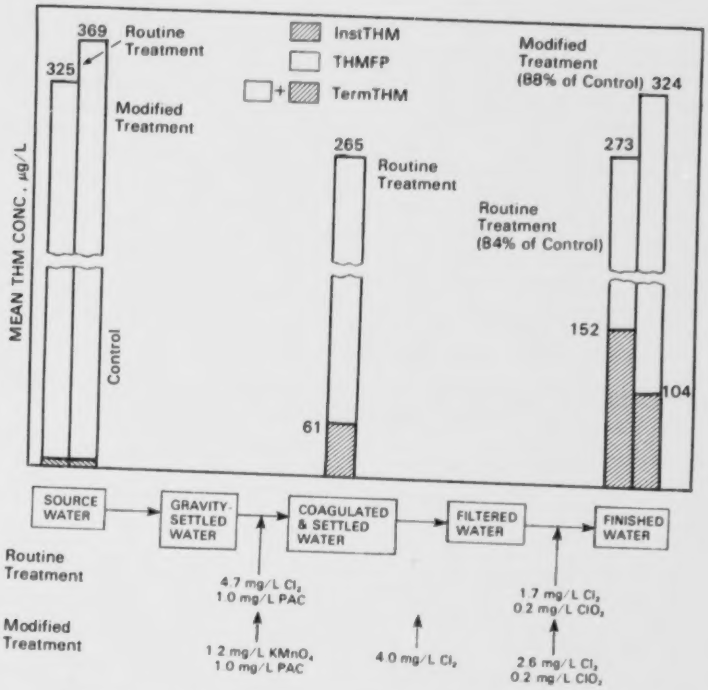


Figure 59. Trihalomethane formation (mean values) during routine and modified (delayed chlorination) treatment at the Wheeling Water Department (WV). (November 1978, 18,000-m³/day [10-mgd] capacity.) THMFP conditions: pH 9.2; 9 to 13°C (48 to 55°F); storage time, 7 days.[18]

treatment, the TermTHM found in the finished water had increased slightly from 84 percent (during routine treatment) to 88 percent of the source water TermTHM, indicating that moving the chlorination point had little effect on this measurement. A decline of 48 µg/L (32 percent) did occur in the finished water InstTHM concentration, however; so moving the chlorination point did have a beneficial effect to some consumers, but this change did not increase precursor removal. Finally, these three studies also confirmed the findings shown in Figure 54 that the ratio of chlorine to bromine in the the trihalomethanes found in the clearwell decreases as precursor is removed. These results indicate again that the conversion of bromide to an active bromine species followed by reaction with precursor materials is a more rapid reaction than the reaction of chlorine with precursors.

Contra Costa, CA, Results—Lange and Kawczynski reported on a full-scale experiment at the Contra Costa Water District to determine the ability of alum coagulation to remove trihalomethane precursors.[20] At this location, the source water is chlorinated during routine treatment to just beyond breakpoint, then coagulated with alum, reducing the pH from 8.2 to 6.9. Lime is added to the settled water to raise the pH to 7.2 before filtering. Following filtration, the pH is adjusted to 8.2, and the water flows into a 1.5 × 10^5 m^3 (40-million-gal) clearwell. The InstTHM concentrations were determined at this point.

When the test began, the plant was operating as noted above, using a coagulant dose of 50 mg/L. The TTHM concentration in the effluent of the clearwell at this time was 273 μg/L. Because source water TermTHM concentrations were not measured in this study, the influence of routine treatment on trihalomethane precursors could not be determined. But a modification to provide chlorination of the settled water lowered the InstTHM concentration in the clearwell effluent from 23 to 37 percent. This result assumes that the 8/15/77 data can be used as a control for the entire experiment (Table 29). Because of the number of variables, exact interpretation of these results is difficult. The increased removal may have been caused by at least three factors, possibly acting together: 1) shorter chlorine contact time before the clearwell sampling point, 2) improved precursor removal prior to chlorination (the purpose of the experiment), and 3) an increase in alum dose from 50 to 80 mg/L over the presumed control. In this study, increasing the coagulant dose did not improve the removal of precursors, as the InstTHM concentrations did not decrease with increasing alum dose in this range.

TABLE 29. INFLUENCE OF SETTLED WATER CHLORINATION ON InstTTHM IN CLEARWELL AT CONTRA COSTA, CA[20]

Date	Alum dose, mg/L	InstTTHM,* μg/L	Percent InstTTHM reduction
8/15/77†	50	273	—
8/22	80	171	37
8/23	80	193	29
9/8	80	231	15
8/25	103	190	30
8/29	120	180	34
8/31	120	185	32
9/13	130	203	26
9/1	148	213	23

*Samples collected after clearwell.
†Control (source water chlorination).

Bristol County Water Company, RI, Results—Blanck reported on the removal of trihalomethane precursors at the Warren Filter Plant of the Bristol County (RI) Water Company.[66] Here, reservoir water receives alum and a coagulant aid before entering a clarifier/flocculator. PAC is then added before the water enters a settling basin. The settling basin effluent receives lime treatment before filtration. Removal of trihalomethane precursors in the settling basin was demonstrated by a decrease in TTHM concentration from 209 to 51 μg/L when chlorination was moved from between the clarifier/flocculator and the settling basin to after the settling basin. This reduction represented a decline of 75 percent. The author did not state, however, where the TTHM samples were collected, or whether they were InstTHM or TermTHM concentrations. In a way similar to the Contra Costa results discussed above, these results are difficult to interpret for cause and effect relationships. Insufficient sampling information is given to control for the influence of a shorter chlorine contact time on the observed results.

Metropolitan Water District of Southern California Results—As reported by Cohen et al., one portion of the Metropolitan Water District of Southern California (MWDSC) system consists of a long transmission line from Lake Mathews to the R.B. Diemer filtration plant, followed by a feeder line to the San Joaquin Reservoir (Figure 60).[80] To assess the ability of the Diemer plant to remove trihalomethane precursors, the trihalomethane concentrations at seven distribution sampling points

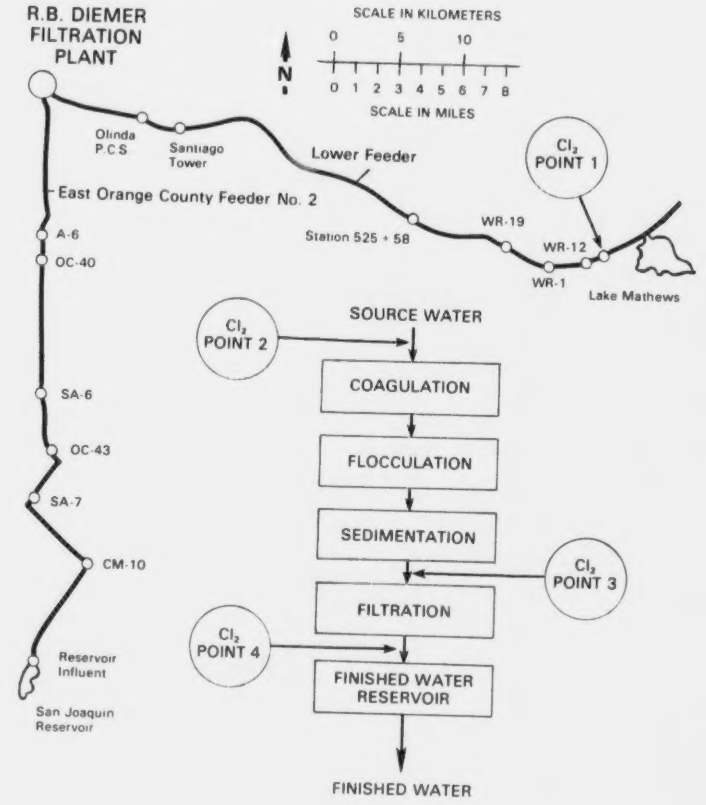

R.B. DIEMER FILTRATION PLANT
SCALE IN KILOMETERS
0
5
10
N
0 1 2 3 4 5 6 7 8
SCALE IN MILES
Olinda P.C.S
Santiago Tower
Lower Feeder
Cl_2 POINT 1
East Orange County Feeder No. 2
A-6
OC-40
Station 525 + 58
WR-19
WR-12
WR-1
Lake Mathews
Cl_2 POINT 2
SOURCE WATER
COAGULATION
SA-6
FLOCCULATION
OC-43
SA-7
SEDIMENTATION
CM-10
Cl_2 POINT 3
FILTRATION
Cl_2 POINT 4
Reservoir Influent
FINISHED WATER RESERVOIR
San Joaquin Reservoir
FINISHED WATER

Figure 60. Sampling and chlorination locations, Metropolitan Water District of Southern California.[80] (Adapted from JOURNAL American Water Works Association, Volume 73, No. 2 [February 1981] by permission. Copyright 1981, the American Water Works Association.)

beyond the Diemer plant shown in Figure 60 were determined. These sampling points were monitored as the point of chlorination was changed in three steps from just after Lake Mathews (point 1, Figure 60) to the filtered water at the Diemer plant (point 4, Figure 60).

Interpretation of the data from this study is complicated by two factors: (1) the two controls, 23 days apart, produced different THM concentrations at the respective sampling points, and (2) chlorine contact times before each sampling point are different for each of the experimental runs, although for this water, THM concentrations reach their maximum concentration in contact times shorter than those experienced during any of the experiments. These factors make comparison of the resulting TTHM data difficult. For this analysis of the data (Table 30), sample point CM-10 was selected, the InstTHM concentrations were assumed to have reached maximum (TermTHM) concentrations, and the control data for 2/8/78 were considered to be correct for comparison with experimental runs 2–4. With these

TABLE 30. REMOVAL OF TRIHALOMETHANE PRECURSORS BY THE R.B. DIEMER FILTRATION PLANT IN THE METROPOLITAN WATER DISTRICT OF SOUTHERN CALIFORNIA[80] *

Date	Chlorination point on Figure 60	Contact time, hr	Free Cl_2 residual, mg/L	TermTrihalomethanes,† µg/L				Term TTHM, µg/L	Percent TermTTHM removal‡
				$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$		
1/16/78	1§	19.6	0.8	6	12	10	<1	28+	—
1/24/78	2	13.2	0.4	9	15	12	4	40	20
1/27/78	3	10.7	0.6	11	12	10	<2	33+	33
2/1/78	4	10.0	0.6	8	14	13	6	41	18
2/8/78	1§	18.7	0.9	15	19	13	3	50	—

*All data are from sampling point CM-10, Figure 60.

†Assumed to be TermTHM concentrations.

‡Based on 2/8/78 data.

§Control.

assumptions, moving the point of chlorination was determined to result in a 20 to 33 percent reduction in TTHM concentrations caused by equivalent removals of precursors in the Diemer plant.

Different assumptions, however, lead to opposite interpretations. For example, selection of the 1/16/78 data for control purposes leads to the conclusion that TTHM's increased as a result of treatment. This demonstrates the difficulty of controlling experiments in real plant situations. Indeed, the investigators of MWDSC concluded that the Diemer plant did not remove precursors and that the change in chlorine application point had no effect on formation of trihalomethanes.

New Orleans, LA, and Evansville, IN, Results—Although control of finished water TermTHM concentrations by removal of precursor during clarification was not the major objective of studies at these two locations, data on the change in TermTHM concentrations through the treatment plant were collected.[63,81] These data (Table 31) show that 40 percent of the trihalomethane precursors were removed by sedimentation in New Orleans, LA, and 31 percent by the entire treatment plant in Evansville, IN.

TABLE 31. PRECURSOR REMOVAL BY COAGULATION/SEDIMENTATION AT TWO FULL-SCALE TREATMENT PLANTS

Location	Mean fraction of precursor removed	Mean fraction converted to InstTHM, C/(C + A)*	Number of tests	Reference
New Orleans, LA	B/(A + B + C)* 0.40	0.28	2	81
Evansville, IN	B′/(A + B + C)* 0.31	0.54	12	63

*Figure 55.

Three studies focused almost exclusively on the impact of moving the point of chlorination on finished water InstTHM and TermTHM concentrations rather than on the removal of precursor by clarification. Because their results are closely related to those previously reported in this subsection, they are reported in the following three subsections.

USEPA In-house Results—USEPA pilot plant studies where chlorine was applied continuously at various points within the treatment train demonstrated the importance of the point of chlorination in causing reduced trihalomethane concentrations in treated water. In one series of experiments, river water was chlorinated (Figure 61, point 1) then held for 2 days to simulate off-stream storage. The water then received either alum or ferric sulfate coagulation, flocculation, sedimentation, and filtration through dual media. A finished water sample was collected and stored for 2 days at 25°C (77°F) before analysis for chloroform. The source water chlorine dose (10 mg/L) was sufficient to maintain a free chlorine residual in the finished water sample for the 2-day contact time.

After 3 days of operation in this mode of treatment, the point of chlorination was moved to the rapid mix, just before the coagulation/flocculation basin (Figure 61, point 2). In the next phase of the study, chlorine was added to the settled water (Figure 61, point 3) to determine whether or not coagulation and precipitation in the settling basin would further reduce the precursor concentration. In the final phase of the study, filtered water (Figure 61, point 4) was chlorinated to determine whether or

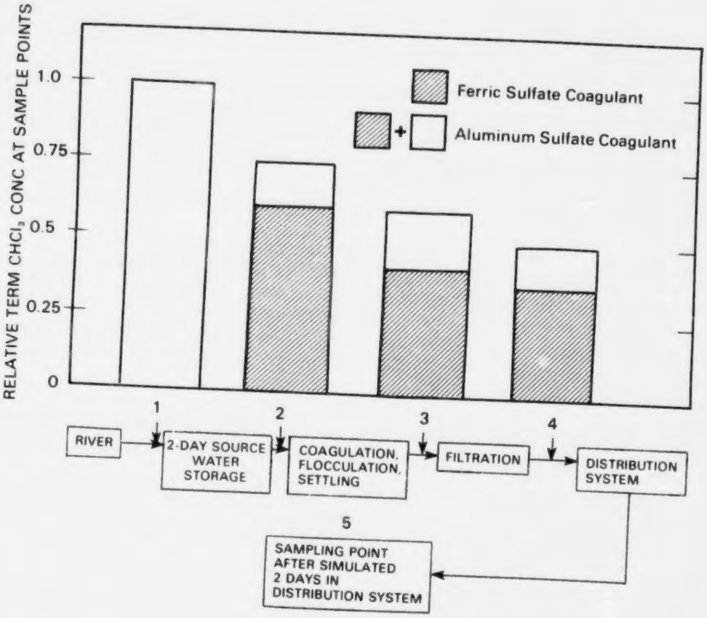


Figure 61. Chloroform in distributed water relative to point of chlorination (pilot plant studies).

not the additional clarification during filtration would further influence the trihalomethane precursor concentration. The last three phases of the study were conducted using ferric sulfate as a coagulant in one case and alum as the coagulant in the other. In each case, the filtered water was stored in bottles at 25°C (77°F) for 2 days to simulate reaching point 5 (Figure 61). This step allowed a comparison of the chloroform concentration theoretically reaching the consumer (Term$CHCl_3$) for the four treatment approaches. Note that routine monitoring of the Ohio River during this period indicated that the TermTHM concentration in the source water did not change significantly during this experiment.

Because a Term$CHCl_3$ concentration was not determined on the actual source water used in this study, the influence of clarification during source water chlorination could not be evaluated; however, the data in Figure 61 do show that if the terminal chloroform concentration during the study of chlorination at point 1 is taken as unity, the removal of chloroform precursor during plain sedimentation, coagulation, and filtration is apparent. This removal is evidenced by the proportionately lower concentration of terminal chloroform resulting when the point of chlorine application was moved from the raw water to the rapid mix (25 percent decline), then to the settled water (40 percent decline), and finally to the filtered water (50 percent decline). Also shown in Figure 61 is the improved effectiveness of ferric sulfate, as opposed to alum, as a coagulant (at least in this water).

The improved effectiveness of ferric sulfate as a coagulant is shown in the last three bars in Figure 61. The differences in the two sets of data occur because, even when chlorine was added at the rapid mix, precursor began to settle in the settling basin and was removed from intimate contact with the free chlorine. Thus even when water is chlorinated at the rapid mix (and all other conditions are equal), a better coagulant will produce a lower terminal chloroform concentration because the separation of chlorine and precursor in the sedimentation basin is hastened.

Cincinnati, OH, Results—The early USEPA experimental results presented in the preceding subsection encouraged the water utility personnel of Cincinnati, OH, to attempt to lower the trihalomethane content in their finished water by moving the point of chlorination from the source water to the clarified water.[82,83] Figure 62 is a schematic diagram of the Cincinnati Water Works. The water is pumped from the Ohio River into two large uncovered reservoirs and retained for approximately 2 days. For several years before this study, the practice had been to add alum to the water going to these reservoirs, along with sufficient chlorine to carry a free residual through the reservoirs, the treatment plant, and the extremities of the distribution system. In mid-July 1975, the point of chlorination was moved from point A to the headworks of the treatment plant (point B, Figure 62). The coagulant (added to the source water) entering the off-stream storage reservoirs (point A) at the time of the study reduced the source water turbidity from approximately 11 to 2 ntu as the water entered the treatment plant.

A sharp decline in tap water chloroform concentration was measured in the distribution system following the movement of chlorine application from point A to point B in mid-July (Figure 63). This decline is attributed to the change in

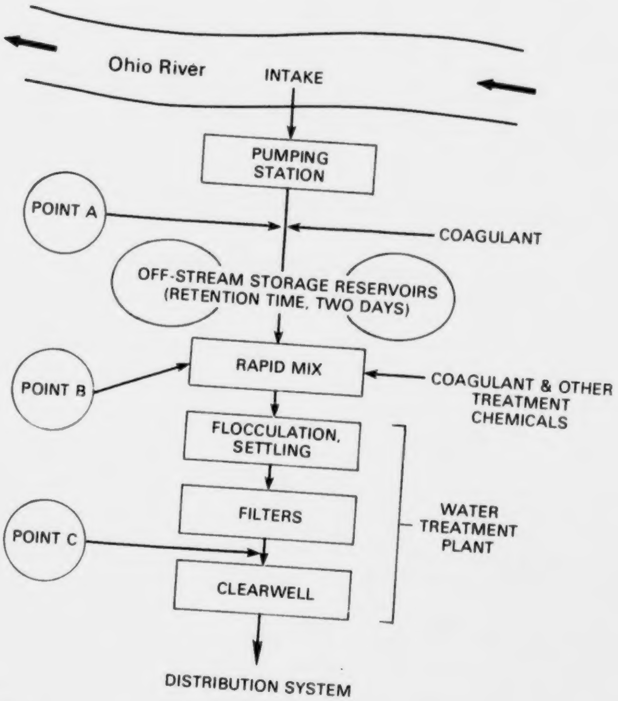

Ohio River
INTAKE
PUMPING STATION
POINT A
COAGULANT
OFF-STREAM STORAGE RESERVOIRS (RETENTION TIME, TWO DAYS)
POINT B
RAPID MIX
COAGULANT & OTHER TREATMENT CHEMICALS
FLOCCULATION, SETTLING
FILTERS
POINT C
CLEARWELL
WATER TREATMENT PLANT
DISTRIBUTION SYSTEM

Figure 62. Schematic diagram of Cincinnati Water Works (OH).[36]

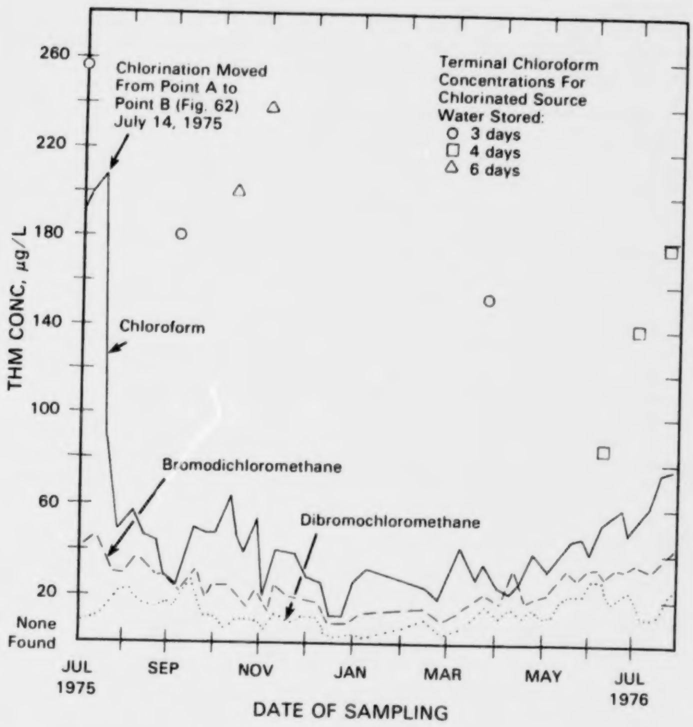


Figure 63. Trihalomethane concentrations in Cincinnati, OH, tap water.[36]

chlorination practice. To determine whether or not changes in the source water had occurred during this time period to account for this decline in chloroform concentration, THMFP determinations were made on the source water at various times during the test period (the recommended control procedure). Although these data are somewhat scattered, they do indicate that the decline in the distributed water chloroform concentration was not caused by a change in the precursor content of the raw river water.

Note that in this case, the ratio of InstTHM to TermTHM in the storage reservoir effluent [the C/(C + A) fraction as shown in Figure 55] was 0.63. Unfortunately, the precursor removal in these off-stream storage reservoirs [the B/(A + B + C) fraction] was not obtained during this study; but a few days before the change, the TermCHCl$_3$ concentration was 260 μg/L in the river and 210 μg/L in the finished water, indicating a 19-percent reduction by the entire treatment process. Note that most of this removal occurred in the storage reservoirs (Table 28). Note also that although a sharp decline in distributed water chloroform concentration occurred, a similar decline in the concentration of the bromine-containing trihalomethanes did not. The reason, as noted previously, is that these materials are formed faster than chloroform and therefore will be formed first from any precursor that remains.

Durham, NC, Results—Young and Singer investigated the removal of trihalomethane precursor at the Durham, NC, Water Treatment Plant.[84] On September 7, 1976, they determined that the chloroform concentration in the source water, Lake Michie, was about 110 μg/L after 2.5 hours of contact with free chlorine. They sampled the clearwell at the water treatment plant 10.35 hours after chlorine was added at the rapid mix on October 16, 1978, and obtained an Inst$CHCl_3$ concentration of 100 μg/L. Because terminal concentrations were not determined on the source and filtered water, the removal of precursor by the treatment plant could not be calculated.

In early January 1977, source water chlorination was stopped, and chlorine was added to the settling basin effluent just before dual-media filtration, 6.25 hours before the sampling point. Before the change, the Inst$CHCl_3$ concentrations in the finished water were about 125 μg/L; immediately after the change, they declined to 75 to 90 μg/L. Because Term$CHCl_3$ concentrations were not determined, the decline in the TermTHM concentrations, if any, could not be calculated. A 28- to 40-percent reduction in Inst$CHCl_3$ concentration in the clearwell (a benefit to consumers near the plant) did occur, however.

Precipitative Softening—Daytona Beach, FL, Results—Another example of the use of clarification for the removal of precursor was a USEPA sponsored study at a softening plant in Daytona Beach, FL.[85,86] Figure 64 is a schematic diagram of the Daytona Beach Water Treatment Plant and shows the two alternative points of application of chlorine during the first two of three modifications. In this system, analyses for InstTHM and TermTHM concentrations were performed on the source water and several hours after filtration (sample point 5).

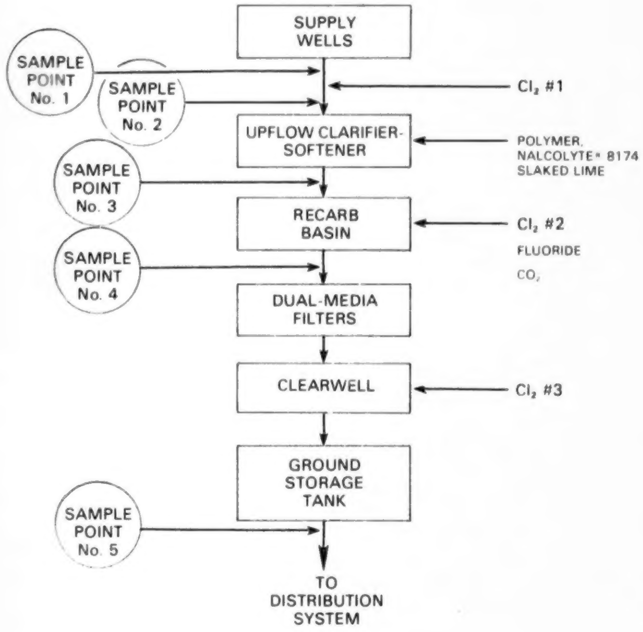

SUPPLY WELLS
SAMPLE POINT No. 1
SAMPLE POINT No. 2
Cl_2 #1
UPFLOW CLARIFIER-SOFTENER
POLYMER,
NALCOLYTE® 8174
SLAKED LIME
SAMPLE POINT No. 3
RECARB BASIN
Cl_2 #2
FLUORIDE
CO_2
SAMPLE POINT No. 4
DUAL-MEDIA FILTERS
CLEARWELL
Cl_2 #3
GROUND STORAGE TANK
SAMPLE POINT No. 5
TO DISTRIBUTION SYSTEM

Figure 64. Flow diagram of the Ralph F. Brennan Water Plant, Daytona Beach (FL).[85,86]

Normal practice consisted of addition of lime and coagulant aid to the upflow softener/clarifier (90-min detention) to increase the pH to about 9.4, followed by recarbonation (when necessary), filtration, and storage in the clearwell. For the third modification of this study, alum (20 to 30 mg/L) was also added at the same point as the lime, and chlorine was added at the clearwell. The TermTHM samples were stored for 2 days at pH 7.2 to 9.6 and a temperature of 25°C (77°F). The large variation in pH makes complete interpretation of the TermTHM data difficult.

During the three treatment modifications, the mean TermTHM concentration of the raw water only changed from minus 7 percent to plus 10 percent of the value measured during routine operation (Figure 65). Comparison of the TermTHM concentration in the source water with that in the finished water revealed a 41-percent decline caused by the precipitative softening and filtration processes. Moving the chlorination point to the recarbonation basin resulted in virtually no change in the percent of source water TermTHM present at sample point 5 (59 percent versus 63 percent). Chlorinating the filtered water did, however, cause a substantial change: Sufficient precursor was removed by filtration to cause an

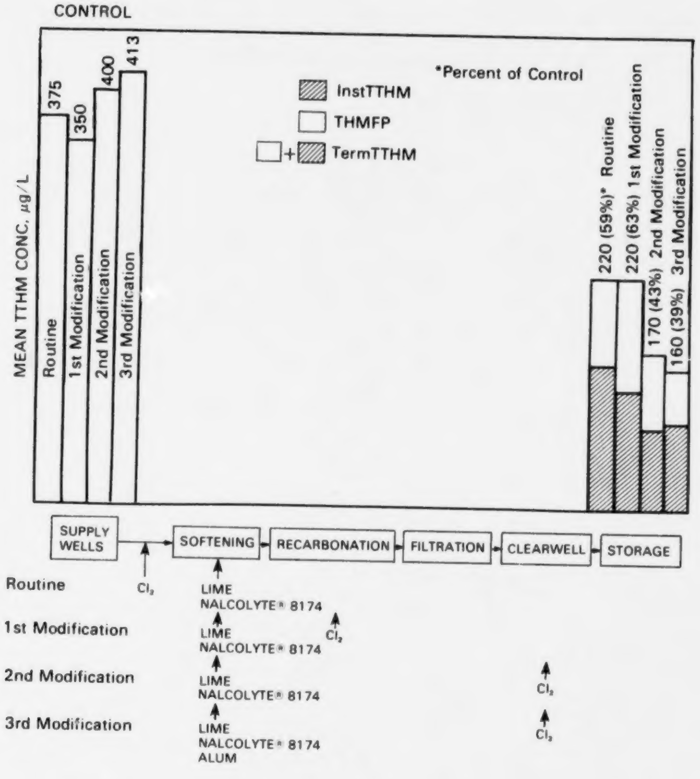


Figure 65. Influence of three treatment modifications to remove trihalomethane precursors at Daytona Beach, FL. THMFP conditions: pH 9.0; 20°C (68°F); storage time, 2 days.[85,86]

additional 16 percent drop in the TermTHM concentration remaining in the finished water. Finally, the addition of alum to the clarifier did not improve the treatment significantly (a 4-percent decrease in source water TermTHM concentration was found in the filtered water). Note that a 33-percent decline in InstTHM concentrations occurred during the second and third modifications (a benefit to consumers near the treatment plant).

In this study, TermTHM concentrations were not measured at the intermediate treatment points, so calculations of the fractions C/(C + A) and B/(A + B + C) (Figure 55) could not be made. But because the high pH (9.3 to 9.5) would increase the formation rate of trihalomethanes, a rather high fraction of source water THMFP would be expected to be converted to InstTHM through the treatment plant [C/(C + A), Figure 55].

Jefferson Parish, LA, and Miami, FL, Results—Although precursor removal by clarification was not the primary objective at these locations, these USEPA sponsored projects evaluated the precipitative softening unit process.[14,87] As was the case in Daytona Beach, these data (Table 32) show the removal of precursor by lime softening in spite of the higher operational pH for this unit process.

TABLE 32. PRECURSOR REMOVAL BY SOFTENING UNIT PROCESSES AT TWO FULL-SCALE SOFTENING PLANTS

Location	Mean fraction precursor removal, B/(A + B + C)*	Fraction converted to InstTHM, C/(C + A)*	Number of tests	Reference
Jefferson Parish, LA	0.16	0.02†	3	14
Jefferson Parish, LA	0.25	0.04†	4	14
Miami, FL	0.29	0.01‡	4	87

*Figure 55.
†Combined chlorine residual maintained through treatment plant; therefore fraction is low.
‡Chlorine first added to settling basin effluent; therefore fraction is low.

Direct Filtration—USEPA In-house Study—The primary objective of this in-house research performed at the USEPA pilot plant facility was to demonstrate the feasibility of direct filtration for the removal of humic substances from water supplies, including their associated total THMFP.[88] In this research, a gravel pit water spiked with humic acid and an algae-laden lake water were used in direct filtration pilot plant studies in which a cationic polyelectrolyte was used as the primary coagulant. Characteristics of the surface waters used are shown in Table 33. Filtration performance was evaluated using classic measures of color, turbidity, and head loss development. In addition, the removal of trihalomethane precursors was evaluated by measuring the THMFP in the raw and filtered waters.

The humic material used in this study was extracted from Michigan peat by soaking it in 0.1N NaOH for 24 hours and recovering it by using the procedure of Hall and Packham.[73] The formation of trihalomethanes from this humic material was evaluated by chlorinating three different solutions with dry-weight humic material concentrations of 2.5, 5, and 8 mg/L, measured as weight on evaporation to dryness. This chlorination was performed in buffered, distilled water using $NaHCO_3$ (12 μmol/L) so that the pH remained approximately constant (8.0 to 8.1). The chloroform yield of 1.3 percent, based on organic carbon (TOC), agreed with the yields generally reported in the literature for humic acid.[15,79,89]

TABLE 33. WATER QUALITY CHARACTERISTICS OF GRAVEL PIT WATERS AND STONELICK LAKE WATER

Water quality parameter	Unspiked gravel pit water*	Spiked humic acid-gravel pit water	Stonelick Lake water†
pH	8.2	8.2	8.0
Turbidity, ntu	1.5	4.0	25
Alkalinity, mg/L as $CaCO_3$	129	NM§	67
Hardness, mg/L as $CaCO_3$	133	NM	110
TOC, mg/L	5.4	6.9	7.3
Suspended solids, mg/L‡	NM	NM	11.2
Apparent color, Pt-Co units	NM	100	340

*Collected 5/18/78.
†Collected 7/11/78.
‡Measured 7/26/78.
§Not measured.

The humic material, about 3.3 mg/L by weight, was added to the gravel pit water for use in the direct filtration pilot plant studies. The gravel pit water was used in this study because it was a low-turbidity water. The unspiked gravel pit water contained 5.4 mg/L of TOC and had a 5-day THMFP concentration of approximately 190 μg/L at pH 8.3 and 25°C (77°F) (Figure 66).

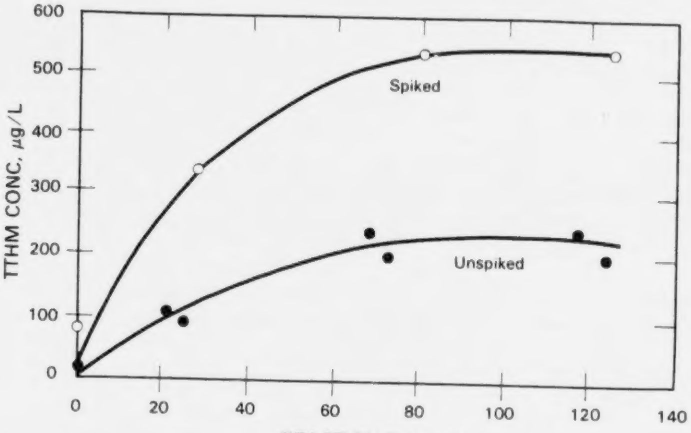


Figure 66. TTHM formation curves for unspiked gravel pit water and spiked humic acid–gravel pit water. pH 8.3; 25°C (77°F).[88]

Jar tests were used to screen cationic polyelectrolytes and to select the dose to be used in direct filtration. The jar tests studied the gravel pit water containing humic materials at approximately the same concentration as was ultimately used in the direct filtration pilot plant studies. Based on the jar test results for pH 6, a dose of 6 mg/L of polyelectrolyte Betz® 1190* was selected as the optimum for destabilization (Figure 67). This dose was used in the direct filtration tests, and the results demon-

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*Manufactured by Betz Laboratories, Trevose, PA 19047.

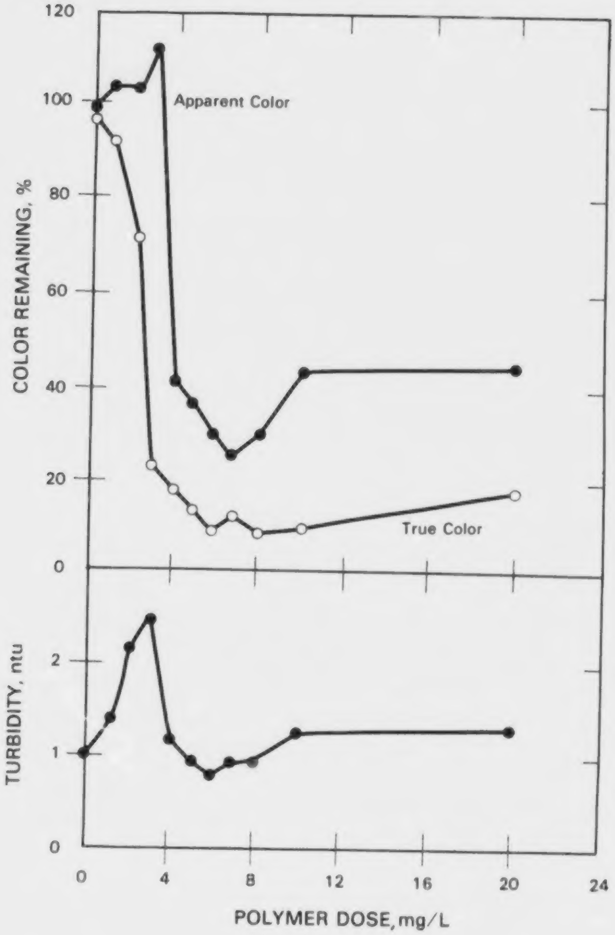

Figure 67. Turbidity and color jar test data for humic acid using Betz® 1190. 5 mg/L humic acid added to gravel pit water; source water color 100 Pt-Co units, pH 6.0; turbidity 1.0 ntu.[88]

strated that jar tests can be used to choose coagulant dosages, even when cationic polymer is the primary coagulant. The cationic polymer selected showed a stoichiometric relationship with respect to doses required to coagulate various concentrations of humic material (Figure 68).

The pilot plant studies using gravel pit water spiked with humic acid demonstrated that direct filtration was effective for turbidity removal (Figure 69). All THMFP analyses were performed at pH 8.3 and 25°C (77°F). The spiked source water had a THMFP concentration of 400 to 470 μg/L; however, as previously noted, approximately 200 μg/L of this was caused by organic compounds that were originally present in the gravel pit water.

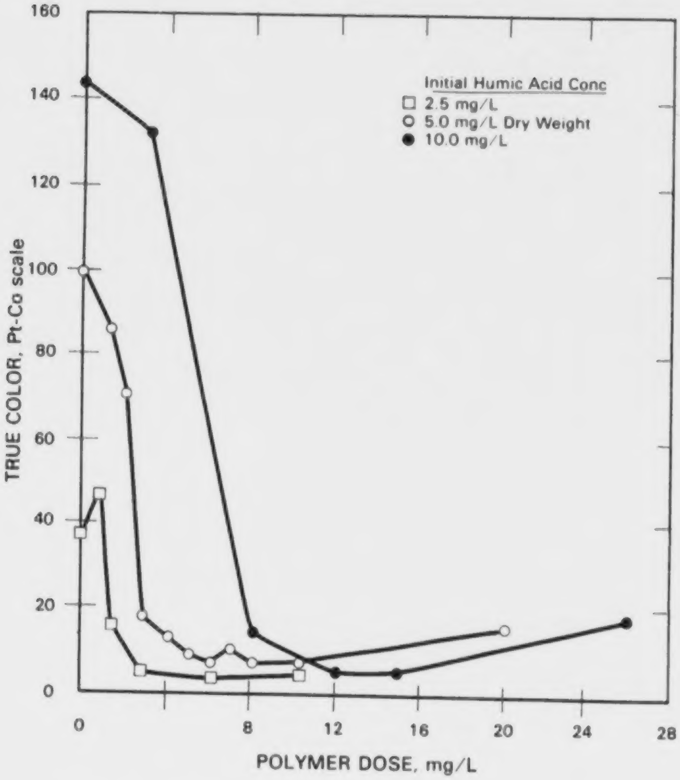

Figure 68. Stoichiometry of coagulation of humic acid with Betz® 1190. Humic acid added to gravel pit water; pH 6.0.[88]

The results of direct filtration runs at pH 6 showed that the THMFP concentration could be reduced to approximately 200 μg/L—the background level of the gravel pit water (Figure 70)—thus demonstrating that humic acid precursors could be removed by direct filtration. As a control, unspiked gravel pit water was filtered at pH 6. In this case, only an average of 9 percent of the trihalomethane precursor material was removed throughout the run, indicating that these materials were very different in character from the spiked humic materials. Furthermore, other tests showed that based on TOC, the chloroform yield of the unspiked gravel pit water was 0.3 percent, again indicating the difference between those precursors and those in the humic materials used for spiking. Finally, the effluent from the filtration test (Figure 70) was evaluated for chloroform yield as a method of organic characterization. Samples collected at 90 minutes and 6 and 10 hours into the filtration test averaged a chloroform yield of 0.4 percent on a TOC basis after 5 days at pH 8.3. Thus the trihalomethane precursors that were not removed in this test were likely to be the same materials that were in the unspiked water. Other treatment processes would therefore be required to remove the organics originally present in the gravel pit water. Note that the data in Figure 71 (page 115) show that better color and THMFP removal occurred at pH 6, in contrast to pH 8.3.

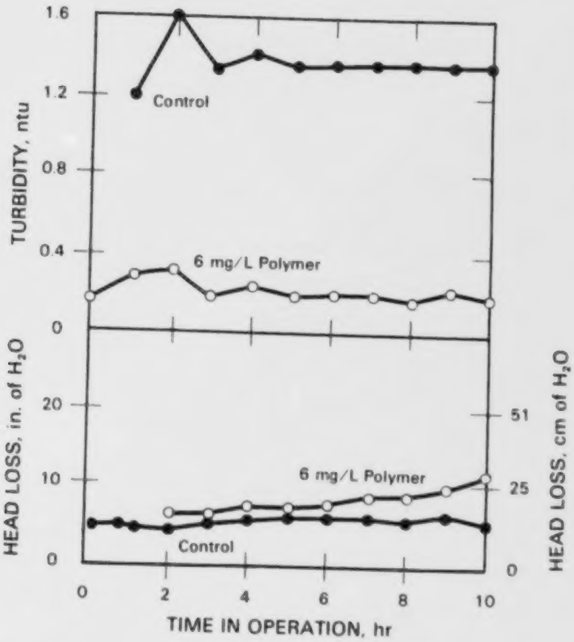

Figure 69. Turbidity and head loss data for spiked humic acid-gravel pit water. Pilot plant operated at pH 6.0; source water turbidity 3.8-4 ntu.[88]

In another phase of the research, water was collected from Stonelick Lake and was used in a brief direct filtration study. This water was selected because of its high apparent color (340 Pt-Co units) and relatively high turbidity (25 ntu). In addition, the trihalomethane precursors in this water represented another type of natural organic material. The organic precursors were assumed to be autochthonous (i.e., produced within the lake from algal activity or from aquatic plants in the littoral zone of the lake). The THMFP for a 5-day contact period at pH 8.3 was 634 μg/L.

Direct filtration using Betz® 1190 as a primary coagulant was effective in terms of color and turbidity removal: Effluent turbidity was generally less than 0.4 ntu, and effluent color was less than 15 units (Pt-Co). Polymer doses required for direct filtration were high because of the high color and turbidity of the raw water. The THMFP data showed that some reduction of the precursors could be achieved by direct filtration (33 to 55 percent reduction in the 5-day THMFP), but the filter effluent THMFP's were still high (Figure 72, page 116).

East Bay Municipal Utility District Results—Carns and Stinson investigated direct filtration following alum coagulation and flocculation at the Walnut Creek Filter Plant of the East Bay Municipal Utility District.[55] In this study, chlorinated water from the Pardee Reservoir arrived at the filter plant containing both InstTHM as well as THMFP. Two test situations were compared with the routine operation. At this plant, alum (17 μg/L) and chlorine are added at the rapid mix, and lime (5 mg/L) is added after the filters. The two test conditions varied from the routine operation by: 1) moving chlorination from the rapid mix to after the filters and, 2) reducing chlorine dose at Pardee Reservoir and chlorination after the filters.

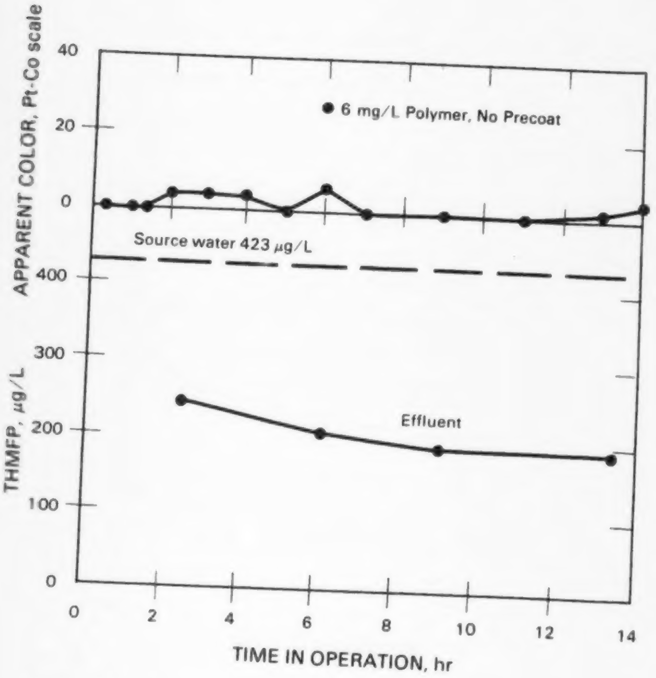

Figure 70. Apparent color and THMFP data for spiked humic acid-gravel pit water. Pilot plant operated at pH 6.0; source water color 85 Pt-Co units. THMFP conditions: pH 8.3; 25°C (77°F); storage time, 6 days.[88]

In this case, during routine operation, the fraction of decline of TermTHM concentration, B′/(A + B + C), was 0.13 during direct filtration. Furthermore the fraction of the THMFP unremoved by direct filtration that was converted to InstTHM during flocculation and direct filtration was 0.25. The data in Table 34 (page 117) show that little change in TermTHM concentration occurred when the chlorination point was moved to after the filter. Also, little effect of change to the "Test 2" conditions was observed. Similarly, in this case, the finished water InstTHM concentration did not decline during either of the test conditions.

Los Angeles, CA, Results—McBride of the Los Angeles Department of Water and Power reported on a pilot plant study in which the 1-hour TermCHCl$_3$ concentration in the source water was compared with the same value after direct filtration.[90] In this case, the TermCHCl$_3$ concentration after 60 minutes was 19 μg/L in the source water, and 10 μg/L after direct filtration. This 47-percent decline in TermCHCl$_3$ thus indicates removal of chloroform precursors during clarification.

Bridgeport, CT, Results—To determine the best technique for treating water in Bridgeport, CT, the Bridgeport Hydraulic Company studied various pilot plant arrangements.[91] Two runs were made with each of these configurations, and the resulting mean TermTHM concentration, turbidity, and color in the finished water were determined (Table 35, page 118). These data show the benefits of precursor removal before disinfection. Compared with the other data presented in this subsection, these removals were high.

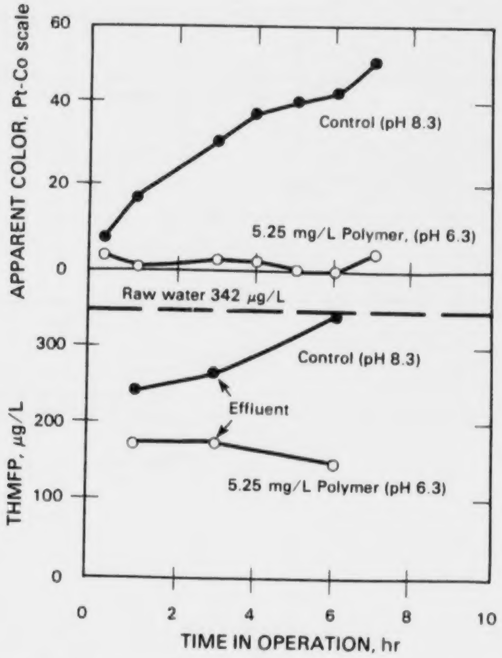

Figure 71. Apparent color and THMFP data for spiked humic acid–gravel pit water. Pilot plant operated at pH conditions indicated; source water color 50–100 Pt-Co units; hydraulic loading, 12 m/hr (5 gpm/ft^2). THMFP conditions: pH 8.3; 25°C (77°F); storage time, 4 days.[88]

Discussion—

Data from 28 different studies discussed in this subsection have demonstrated the potential for removing trihalomethane precursors by clarification. Because precursors are not defined organic chemicals, but a mixture of compounds that varies from location to location, the potential for removing these materials by clarification also varies from location to location.

Table 36 (page 119) summarizes the data on trihalomethane precursor removal from all the studies presented in this subsection. Although experimental design problems or incomplete data reporting made some interpretations difficult, for 24 of the 28 studies, calculations could be made indicating the effectiveness of the clarification process. Trihalomethane precursor removals varied from 16 to 51 percent for coagulation/sedimentation plants, from 16 to 41 percent for precipitative softening plants, and from 13 to 100 percent for direct filtration plants. In each case, these removals quantify the decline in TermTHM concentrations that could be attributed to the presence of a given treatment plant or unit process. If the water had not been so treated, consumers would have had higher trihalomethane concentrations in their drinking water.

Because clarification processes can remove trihalomethane precursors, the possibility exists for lowering trihalomethane concentrations even further by chlorinating after the clarification processes. By determining the concentrations of

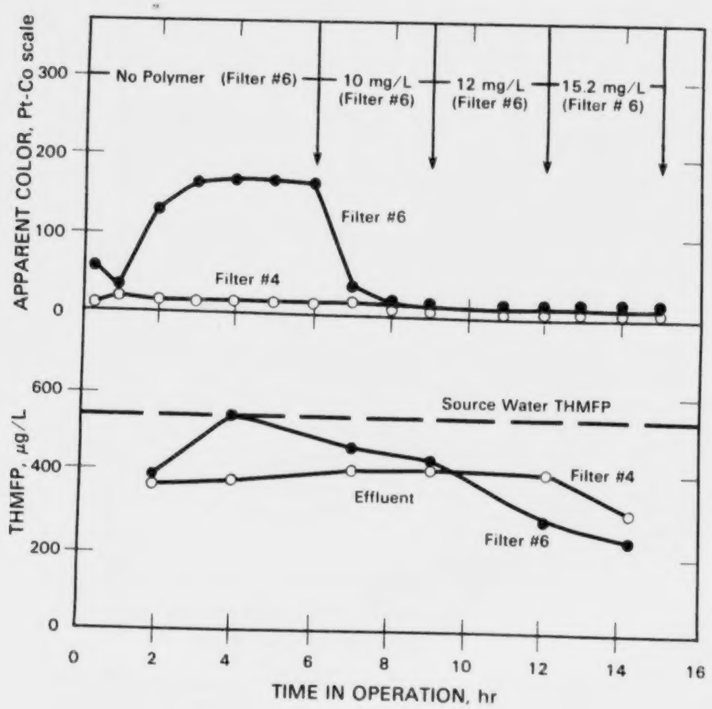

Figure 72. Apparent color and THMFP data for Stonelick Lake water. Pilot plant operated at pH 6.0, filter 4, polymer dose of 17.9 mg/L; filter 6, polymer dose indicated between arrows; source water color 225 Pt-Co units; hydraulic loading 5 m/hr (2 gpm/ft²). THMFP conditions: pH 8.3; 25°C (77°F); storage time, 5 days.[88]

TermTHM and InstTHM and calculating the THMFP at various points in a treatment plant, predictions for the potential success of lowering trihalomethane concentrations by moving the point of chlorination in that location can be made. The chance of success is enhanced if the fraction of TermTHM removed in the clarification or precipitative softening step and the fraction of precursor converted to InstTHM through the unit process is high. Under such circumstances, the TermTHM concentrations in the finished water are likely to be lowered if the chlorination point is located after the unit process under study. In nine of the 28 studies reported in Table 36, the fraction C/(C + A) from Figure 55 could be calculated and compared with the observed change in TermTHM concentration when the chlorination point was moved. In the seven of those nine cases where source water was chlorinated to produce a free residual, this fraction ranged from 0.05 to 0.63. Only when C/(C + A) was 0.63 did a significant decline in finished water TermTHM occur when the chlorination point was moved. This result verifies that this fraction must be high through a unit process to lower TermTHM concentrations successfully when chlorination is moved to a point after that unit process. Unfortunately, insufficient data are available to make a numerical judgment about

TABLE 34. REMOVAL OF TRIHALOMETHANE PRECURSORS BY COAGULATION AND DIRECT FILTRATION AT THE WALNUT CREEK PLANT OF THE EAST BAY MUNICIPAL UTILITY DISTRICT[55]

	Source water from Pardee Reservoir				Clearwell water		
Test	Cl_2 residual, mg/L	InstTHM, µg/L	THMFP,* µg/L	TermTHM* µg/L	InstTHM, µg/L	THMFP,* µg/L	TermTHM,* µg/L
Control	0.21	84	63	147	95	33	128
Test 1†	0.21	95	52	147	93	35	128
Test 2‡	0.14	84	65	149	94	16	110

*2 days, pH 9.2.
†Filtered water chlorination.
‡Reduced chlorination at Pardee Reservoir and filtered water chlorination.

TABLE 35. INFLUENCE OF VARIOUS CLARIFICATION TECHNIQUES ON TRIHALOMETHANE PRECURSOR REMOVAL AT BRIDGEPORT, CT[91]

	Percent removal		
Treatment	Mean TermTHM*	Turbidity	Color
Chlorine, lime, fluoride, Virchem® (control)	0	0	21
Direct filtration, post-chlorination:			
Run 1	36	86	89
Run 2	54	88	93
Conventional treatment, post-chlorination:			
Run 1	54	86	89
Run 2	54	88	94
O_3/diatomaceous earth filtration, post-chlorination:			
Run 1	64	87	81
Run 2	73	75	80

*Storage conditions not specified.

the size of the fraction C/(C + A) needed to lower TermTHM concentrations following a chlorination move. This is also true regarding the fraction B/(A + B + C) or B′/(A + B + C).

Also, if the rate of formation of trihalomethanes is favorable in a specific location, shortening the time elapsed between chlorination and the finished water by moving the chlorination point downstream in the treatment plant will probably lower the InstTHM concentration in the finished water, thereby benefiting consumers (especially those near the treatment plant) (Figure 56). As shown in Table 36, 10 locations attempted to control trihalomethane concentrations by moving the chlorination point. Seven produced a positive reduction of 2 to 75 percent in finished water InstTHM concentration.

As noted in Section V, studies such as these should involve sufficient samples to monitor changes in source water precursor concentrations and to ensure that apparent changes in precursor concentration cannot be attributed to analytic imprecision. Composite sampling may also prove to be beneficial toward this end. Although some of the 28 studies discussed may have been based on fewer samples than desirable, taken together they demonstrate well the partial removal of precursor by clarification. Additionally, the studies described were generally performed over a short time. Studies should be performed over at least a 1-year period to determine seasonal effects on precursor concentration, nature of the precursor, and effects of seasonally varying reaction conditions (if not held constant) on the results observed.

Finally, if precursor is removed by clarification or precipitative softening, bromine-containing trihalomethane concentrations will be influenced less than the chloroform concentration. The reason is that chlorine reacts quickly with any bromide present in the water to produce active bromine species that effectively compete for whatever precursor remains after treatment. This effect will be most pronounced early in the chlorine/precursor reaction, declining as time passes and more chloroform is formed, until precursor is exhausted.

Note that for several of the 10 utilities that moved the point of chlorination in an attempt to lower trihalomethane concentrations (Table 36), data on the resulting bacteriologic quality of the finished water were also collected. Where available, these data will be discussed in Section IX.

TABLE 36. SUMMARY OF DATA ON REMOVAL OF TRIHALOMETHANE PRECURSORS BY CLARIFICATION

Treatment and location	Percent TermTHM reduction during clarification	Fraction C/(C + A)†	Influence of moving chlorination to later point in treatment train		Remarks	Reference
			Percent InstTHM reduction	Percent increased* TermTHM reduction		
Coagulation and settling, and coagulation-settling-filtration:						
Huntington, WV	29[a]	‡	§	§	[a]Fraction B′/(A + B + C) from Figure 55	18
Fox Chapel, PA	49[a]	‡	§	§	[a]Fraction B′/(A + B + C) from Figure 55	18
Wilkinsburg-Pennsylvania Joint Water Authority, PA	38[a]	‡	§	§	[a]Fraction B′/(A + B + C) from Figure 55	18
Evansville, IN	36[a]	‡	§	§	[a]Fraction B′/(A + B + C) from Figure 55	18
Pittsburgh, PA	38[a]	‡	§	§	[a]Fraction B′/(A + B + C) from Figure 55	18
Western Pennsylvania Water Co., Hays Mine Plant, PA	35[a]	‡	§	§	[a]Fraction B′/(A + B + C) from Figure 55	18
Beaver Falls, PA	33[a]	‡	§	§	[a]Fraction B′/(A + B + C) from Figure 55	18
Wheeling, WV	30[a]	‡	§	§	[a]Fraction B′/(A + B + C) from Figure 55	18
Cincinnati, OH	51[a]	‡	§	§	[a]Fraction B′/(A + B + C) from Figure 55	18
Louisville, KY	28[a]	‡	§	§	[a]Fraction B′/(A + B + C) from Figure 55	18
Cincinnati, OH	>33[a]	0.26	39[b,c]	0[b]	[a]Fraction B′/(A + B + C) from Figure 55 [b]Chlorine moved to settled water; [c]May have been influenced by a sharp decline in source water precursor during the study period	18
Pittsburgh, PA	26[a]	0.05	54[b]	0[b]	[a]Fraction B′/(A + B + C) from Figure 55 [b]Chlorine moved to settled water	18
Wheeling, WV	16[a]	0.23	32[b]	0[b]	[a]Fraction B′/(A + B + C) from Figure 55 [b]Chlorine moved to settled water	18
Contra Costa, CA	‡	‡	23 to 37[a]	‡	[a]Chlorine moved to settled water	20
Bristol, RI	‡	‡	75[a,b]	‡	[a]Chlorine moved to settled water [b]Data assumed to be InstTHM concentrations	66

Continued

TABLE 36. (Continued)

Treatment and location	Percent TermTHM reduction during clarification	Fraction C/(C + A)†	Influence of moving chlorination to later point in treatment train: Percent InstTHM reduction	Influence of moving chlorination to later point in treatment train: Percent increased* TermTHM reduction	Remarks	Reference
Metropolitan Water District of Southern California	20[a]	‡	‡	0[b]	[a]Fraction B′/(A + B + C) from Figure 55 [b]Chlorine moved to filtered water	80
New Orleans, LA	40[a]	0.28			[a]Fraction B/(A + B + C) from Figure 55	81
Evansville, IN	31[a]	0.54			[a]Fraction B′/(A + B + C) from Figure 55	63
USEPA Pilot Plant	‡	‡	‡	40[a]	[a]Chlorine moved to settled water	
Cincinnati, OH	19[a]	0.63	‡	86[b]	[a]Fraction B′/(A + B + C) from Figure 55 [b]$CHCl_3$ only; chlorine moved to off-stream reservoir effluent	82, 83
Durham, NC	‡	‡	28 to 30[a]	‡	[a]Chlorine moved to settled water	84
Precipitative softening:						
Daytona Beach, FL	41[a]	‡	10[b], 33[c,d]	0[b], 23[c,d]	[a]Fraction B′/(A + B + C) from Figure 55 [b]Chlorine moved to settled water [c]Chlorine moved to filtered water [d]Varying pH storage conditions influenced results	85, 86
Jefferson Parish, LA	16 to 25[a]	0.02 to 0.04[b]	§	§	[a]Fraction B/(A + B + C) from Figure 55 [b]Chloramine residual	14
Miami, FL	29[a]	0.01[b]	§	§	[a]Fraction B/(A + B + C) from Figure 55 [b]Chlorine routinely added to settled water	87
Direct Filtration:						
USEPA Pilot Plant	35 to 100[a,b]	‡	§	§	[a]Spiked water reduced to starting concentration [b]Fraction B′/(A + B + C) from Figure 55	88
East Bay MUD, CA	13[a]	0.25	2[b]	0[b]	[a]Fraction B′/(A + B + C) from Figure 55 [b]Chlorine moved to filtered water	55

Continued

TABLE 36. (Continued)

Treatment and location	Percent TermTHM reduction during clarification	Fraction C/(C + A)†	Influence of moving chlorination to later point in treatment train		Remarks	Reference
			Percent InstTHM reduction	Percent increased* TermTHM reduction		
Los Angeles, CA	47[a]	‡	§	§	[a] Fraction B′/(A + B + C) from Figure 55	90
Bridgeport, CT	36 to 54[a]	‡	§	§	[a] Fraction B′/(A + B + C) from Figure 55	91

*Increase compared with reduction that occurred with routine operation.

†From Figure 55.

‡Unknown.

§Not attempted.

Control of Precursors at the Source

General Considerations—

When possible, water utilities should examine the quality of their source water to determine whether or not operational changes could be made to improve the quality and thereby lower the concentration of trihalomethane precursors. Some examples of this technique will be given in the following subsections.

Experimental Results—

Selective Withdrawal from Reservoirs—Barnett and Trussell reported on the experiences of the Casitas Municipal Water District.[92] This water district uses Lake Casitas as its source, with a maximum depth at the intake of 59 m (194 ft) and a volume of 308×10^6 m^3 (254,000 acre-ft). Water can be withdrawn from the lake through any one of nine hydraulically operated intake gates that are separated by depth intervals of 7.3 m (24 ft). During the period August 1977 to March 1978, the organic content of the lake waters was measured at the surface and at 23, 46, and 58 m (75, 150, and 191 ft). Samples were analyzed for TOC concentrations and 100-hour THMFP; temperature and pH were not reported. Analyses completed during that period indicate that both concentrations for TOC and total THMFP at a given depth in the lake vary significantly from time to time during the year. Several factors have been identified that appear to influence these concentrations. These are summarized as follows:

1. Natural conditions that cause thermal and dissolved oxygen stratification and turnover of the lake. Data collected during January and February 1977 indicate that upwelling of a very small zone of anaerobic water during turnover caused a major increase in total organic content of the source water. A TOC concentration of 9.3 mg/L was found during this period—a higher concentration than occurred previously.
2. The Lake Casitas aeration system that is in operation during the period April to October of each year. This system significantly influences thermal and dissolved oxygen stratification patterns.
3. Algal blooms.
4. Unusually large quantities of inflow to the lake from the Casitas watershed, resulting in inundation of areas that have not been previously covered by water.

Figure 73 illustrates the importance of these factors. The organic profile collected on August 25, 1977, showed that (at least in this case) significantly lower concentrations of trihalomethane precursors existed in the zone of the lake from a depth of 30 to 50 m (100 to 165 ft). Water drawn from this zone would be expected to have considerably lower TermTHM concentrations upon chlorination than if source water had been drawn from other levels in the lake. This experience illustrates a practical technique that a water utility may have at its disposal for controlling trihalomethane precursors in their source water.

Plankton Control—Recently, investigators have been studying the possibility that algae (either themselves or their extracellular products) can act as trihalomethane precursors. Experiments in 1976 and 1977 showed that constituents of both centrifuged cells and the noncentrifugeable extracellular products from a culture of the blue-green algae *Anabaena flos-aquae* and the green algae *Panadorina morum* served as trihalomethane precursors when these materials were chlorinated (Unpublished report. R. Daum, USEPA, Cincinnati, OH, 1979). Later, Hoehn et al. conducted a laboratory study of the trihalomethane yield capacity (a version of THMFP) of algal-produced organic carbon.[93] This study was undertaken after a possible causal relationship was observed in 1975 between the trihalomethane concentrations in the finished water of the Fairfax County Water Authority and chlorophyll-*a* concentrations in the source water for that utility. From this study, the authors concluded:

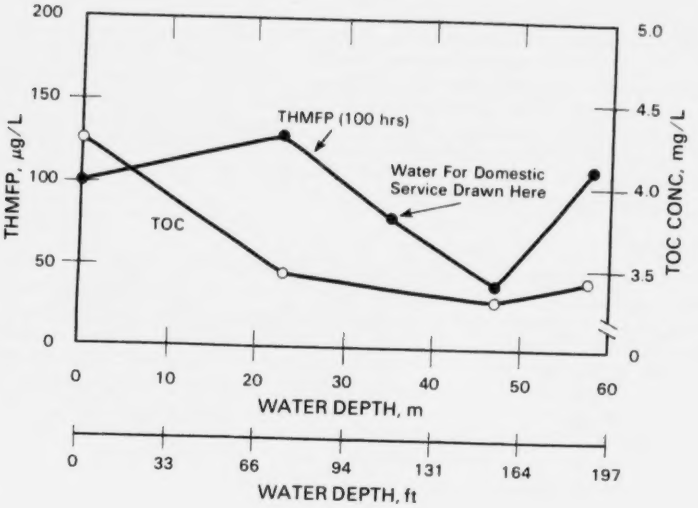

Figure 73. Lake Casitas organic profile, August 25, 1977, Casitas Municipal Water District (CA).[92] (Adapted from JOURNAL American Water Works Association, Volume 70, No. 11 [November 1978] by permission. Copyright 1978, the American Water Works Association).

1. Both green algae and blue-green algae produce extracellular products that upon chlorination yield at least as much chloroform per unit of organic carbon as has been reported from chlorination of humic and fulvic acids.
2. The algal extracellular products generally produce greater yields of chloroform from the available TOC than does the algal biomass.
3. Though not yet fully confirmed, indications are that high-yielding trihalomethane precursors are liberated from algae in greater abundance near the end of the exponential phase of growth than at any other time during their life cycle.
4. Data collected during 1976 and 1977 do not confirm the apparent causal relationship observed in 1975 between finished water trihalomethane concentrations and reservoir chlorophyll-*a* concentrations.

Finally, work by Briley et al. confirmed that high concentrations of trihalomethane are produced from algal biomass and algal metabolites.[94] They also found that both algae and extracellular products derived from algae growth produced trihalomethane concentrations that are comparable to yields observed from humic and fulvic acids. In contrast to the work of Hoehn et al.,[93] Briley et al.[94] suggest that maximum levels of trihalomethanes appear to be produced during the entire exponential growth phase of *Anabaena.*

The significance of these results is that a reduction of trihalomethane concentrations may be partially accomplished by controlling the natural phytoplankton communities in the water source, particularly if source water chlorination is practiced. Several techniques, the most popular of which is treatment with copper sulfate, are available for controlling algal populations in lake and reservoir waters.

Prevention of Salt Water Intrusion—The data from Lange and Kawczynski show that in Contra Costa, CA, sea water intrusion during a drought caused the bromide content of the source water to increase.[20] This increase in bromide content caused consistently higher yields of trihalomethanes (Figure 5, Section III) and aggravated attempts to control trihalomethanes because of the faster formation rates of bromine-containing trihalomethanes. Although in this case the end of the drought caused the source water quality to return to normal, water utility personnel faced with a continually increasing sea water intrusion problem might consider the development of an underground fresh water barrier created by injection wells or spreading basins as one technique to reduce the type and concentration of TTHM's in their chlorinated finished water.

Discussion—

Utility managers should carefully consider the potential for altering the quality of their source water to lower trihalomethane precursor concentrations reaching the treatment plant. Periodic determinations of source water trihalomethane precursor concentrations (THMFP) may reveal control measures that could be taken to minimize these concentrations. These measures may include control of algae, prevention of salt water intrusion, or selected uses of alternative sources. When alternative sources of water are considered, THMFP determinations should be carried out over the range of conditions likely to be present in the distribution system to verify conclusions drawn about effect of changes in source water quality on the ultimate trihalomethane content of distributed water.

Aeration

General Considerations—

Because the primary trihalomethane precursors are now understood to be high-molecular-weight humic and fulvic acids, aeration would not be expected to be effective for precursor removal. Nevertheless, aeration was briefly evaluated in-house by USEPA for reducing THMFP in Ohio River water.

Experimental Results—

With the use of the diffused-air aerator described in Section VI, Subsection Aeration (Experimental Results), river water was aerated at varying air/water ratios, then chlorinated and stored at 25°C (77°F) for 2 days in sealed vessels. A companion river water sample was chlorinated and stored under the same conditions without being aerated. The data in Table 37 show the influence of aeration on THMFP to be insignificant (less than 10 percent), even at an air/water ratio of 20/1. As shown earlier in Figure 52, the chloroform formation potential also remained in an aerated tap water sample.

Discussion—

As would be expected, this technique is not effective for trihalomethane precursor removal.

Oxidation

General Considerations—

Several oxidants have been investigated by USEPA and others to determine whether or not they would be effective in oxidizing precursor material and thereby reducing the trihalomethane concentration after chlorination. The oxidants studied were ozone, chlorine dioxide, potassium permanganate, ozone/ultra-violet radiation, and hydrogen peroxide.

Two goals are desirable when these oxidants are applied: 1) the stated objective of lowering THMFP by chemically altering the precursor materials, and 2) complete chemical oxidation of the precursors (to carbon dioxide) to eliminate the potential problem of the presence after treatment of oxidation byproducts possibly more

TABLE 37. EFFECT OF AERATION (10-MINUTE CONTACT TIME) ON REDUCING THMFP

Type of water	Air/water ratio (V/V)	Trihalomethanes, µg/L after 2-day contact time at 25°C (77°F)				TermTTHM, µg/L
		$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	
Ohio River water	—	NF[*]	NF	NF	NF	NF
Ohio River water with 13 mg/L Cl_2 (control)	—	66	28.0	8.0	<0.1	102
Aerated[†] Ohio River water	1:1	66	27.8	8.0	<0.1	102
Aerated Ohio River water	4:1	64	26.8	6.6	<0.1	97
Aerated Ohio River water	6:1	62	25.8	7.6	<0.1	95
Aerated Ohio River water	8:1	62	26.8	7.8	<0.1	97
Aerated Ohio River water	10:1	59	25.6	7.7	<0.1	92
Aerated Ohio River water	20:1	61	26.0	8.0	<0.1	95

[*] None found.

[†] Activated-carbon-filtered air.

harmful than the trihalomethanes. As will be seen below, the first of these goals is accomplished to some degree in some cases. The second goal is not usually accomplished, which indicates that oxidation byproducts remain in the treated water. Comparatively little is now known about the nature of these materials, but this information can be found summarized later in Section VIII, Alternative Disinfectants.

The results summarized below mainly indicate the potential of oxidation techniques for achieving the goal of lowering THMFP.

Experimental Results—

Ozone—The USEPA in-house studies used the ozone contactor described in Section VI, Subsection Oxidation. In the continuous-flow studies, unchlorinated Ohio River water was coagulated, settled, and filtered before ozonation. Three different applied ozone doses were used at a constant 5- to 6-minute contact time. Following ozonation, the samples were chlorinated and stored for 6 days at 25°C (77°F).

Ozonating for a few minutes' contact time with small dosages followed by chlorination produced slightly more chloroform and TTHM's than with chlorination alone (Table 38). This means that the THMFP was not reduced by low-level ozonation, and subsequent chlorination to produce a disinfectant residual in the distribution system would result in trihalomethane production. The reason that low-level ozonation plus chlorine produced more chloroform than chlorination alone is not known, but the effect has been seen by others. Possibly because the ozone satisfies some of the oxidant demand, more chlorine is available for the trihalomethane reaction. But because of the high chlorine dose used (8 mg/L), this explanation does not seem likely, and a change in the organic precursors must be assumed. The reduction in bromine-containing trihalomethanes is probably caused by oxidation of bromide to some nonreactive species (possibly bromate) by the ozone.[24,25] The applied ozone dose of 227 mg/L may have completely oxidized some of the trihalomethane precursors, thereby reducing the chloroform formation potential from 91 to 62 µg/L (32 percent), and the TermTTHM by 43 percent.

To observe the effect of longer contact times and generally higher ozone doses, the ozone contactor was used as a batch reactor in a second test rather than a continuous, countercurrent reactor, as in previous runs. The THMFP of Ohio River water can be reduced by ozone (Figure 74), but the contact time is probably unrealistic for water treatment (several hours). The ozone application rate for this batch study was 43.5 mg O_3/minute applied to approximately 13 liters of river water,

TABLE 38. EFFECT OF OZONATION ON THMFP*

Test	Applied† O_3 dose, mg/L	Chlorine dose after O_3 treatment, mg/L	Trihalomethanes, µg/L				Term TTHM, µg/L	Percent TermTTHM removal
			$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$		
1	0‡	8	6	14	4	NF§	24	—
	0.7	8	15	8	3	NF	26	-8
2	0‡	8	12	9	2	NF	23	—
	18.6	8	14	8	8	NF	30	-30
3	0‡	8	91	26	6	NF	123	—
	227	8	62	7	1	NF	70	43

*Stored for 6 days at 25°C (77°F). Dual-media filter effluent; continuous-flow studies; 5- to 6-minute contact time.

†Applied dose, continuous-flow studies, mg/L =

$$\frac{\text{mg } O_3}{\text{standard liter of gas } (O_3 + O_2)} \times \frac{\text{standard liters of gas } (O_3 + O_2)}{\text{minute}} \times \frac{\text{minute}}{\text{liters of water}}$$

‡Control.

§None found.

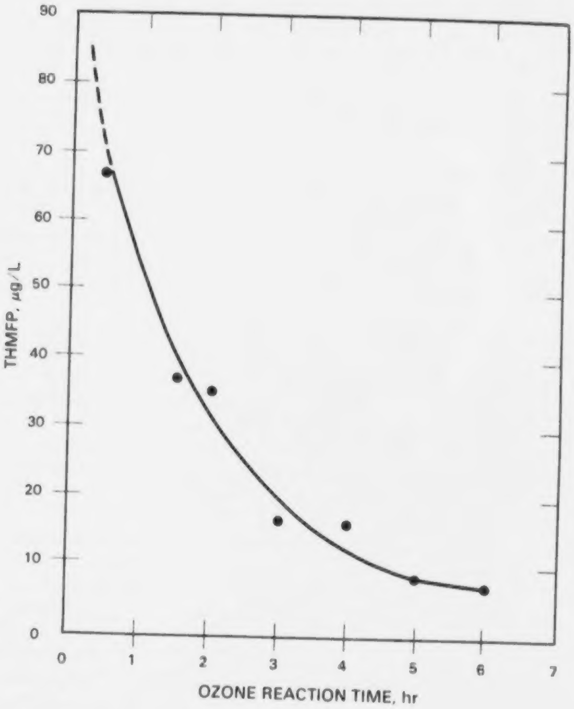

Figure 74. Batch treatment of Ohio River water with ozone. 13-L batch reactor; 3.3 mg O_3/L/min. THMFP conditions: pH not reported; 25°C (77°F); storage time, 6 days.

or about 3.3 mg O_3/L per minute. In this batch test, the calculated gas/water ratio for the 6-hour contact time is approximately 14:1; therefore, the observed effect was caused by ozone oxidation and not merely gas stripping, as aeration alone at a 20:1 air/water ratio was ineffective for reducing the THMFP concentration (Table 37).

Glaze et al. studied the potential of ozone for oxidation of trihalomethane precursors in Texas lake water.[40] An example of their findings using a 22-liter batch reactor and three different ozone doses is shown in Figure 75. With sufficient exposure to ozone, substantial removal of trihalomethane precursor occurred. As in the USEPA in-house study (Table 38), an initial drop in precursor concentration was followed by an increase with a small additional amount of ozonation, which was followed by a further decline when more ozone was applied.

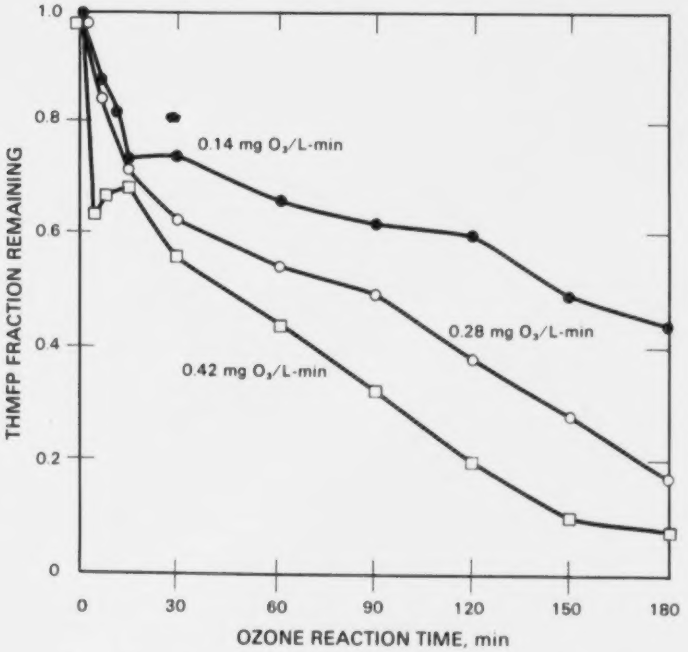

Figure 75. Ozone destruction of trihalomethane precursors in Caddo Lake, TX, water. THMFP conditions: pH 6.5; 26°C (79°F); storage time, 3 days.[40]

To confirm these results, Glaze et al. assumed the initial rate of precursor disappearance to be exponential and subtracted this projected decay curve from the actual data. The plot of this difference showed the appearance and then destruction of a material called "byproduct precursor" by these workers (Figure 76). A similar result was shown by Riley et al.[95] (Figure 77), but because their samples were stored for the determination of TermTHM concentrations at different pH values, their results are difficult to interpret precisely.

To determine what success other investigators have had in oxidizing trihalomethane precursors, Trussell[25] and Trussel and Umphres[24] reviewed the literature and found eight references to this type of work. These data (Table 39) show great variation in performance, but this is not surprising because of the variations in

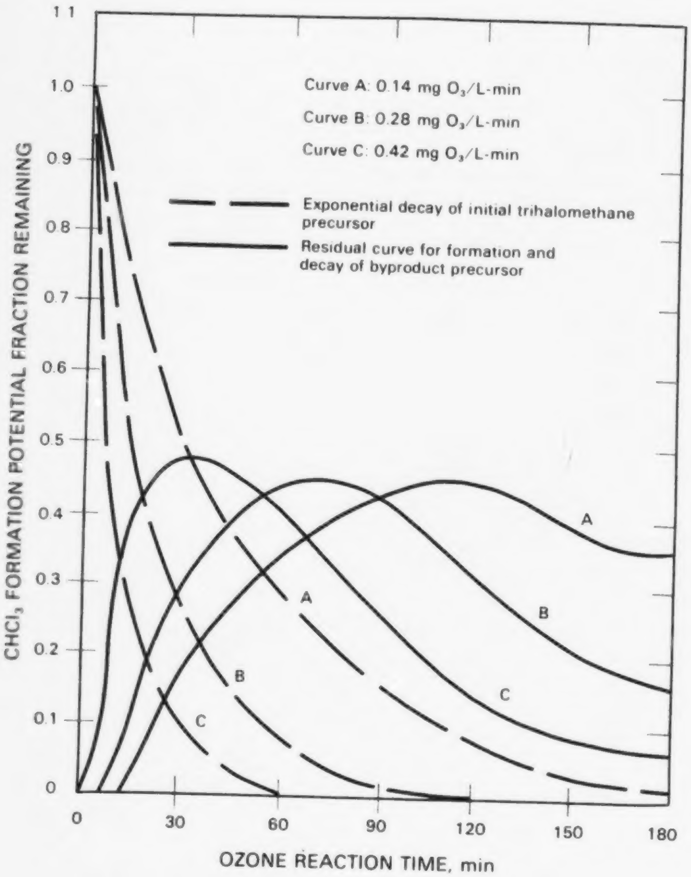

Figure 76. Analysis of THMFP destruction curves for Caddo Lake, TX, water.[40]

experimental conditions among these studies—not the least of which are the conditions under which TermTHM's are measured. Taken in the aggregate, however, the data do indicate the potential of trihalomethane precursor oxidation by ozone for prevention of formation of trihalomethanes even though ozone doses and contact times much higher than those used for disinfection may be required.

Chlorine Dioxide—Miltner investigated the effect of chlorine dioxide on trihalomethane precursors with both raw Ohio River water and prepared humic acid mixtures.[39] In the first part of the study, raw Ohio River water was divided into two samples, one of which was treated with 2 to 3 mg/L chlorine dioxide generated by the method of Granstrom and Lee.[96] Both samples were stored for 48 hours, after which aqueous chlorine was added to both samples. During the 48-hour storage period, the chlorine dioxide was consumed by the raw water.

The results of this experiment show that chlorine dioxide was altering the precursor, because chlorination of the chlorine dioxide-treated water resulted in

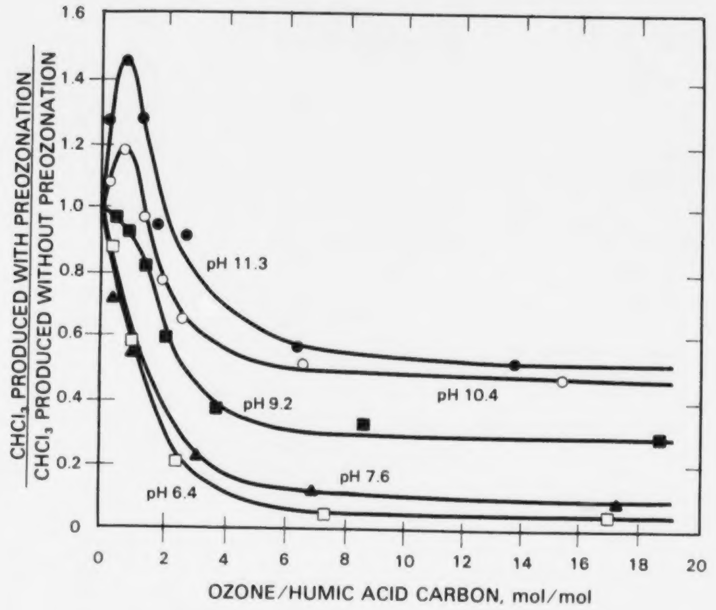

Figure 77. The influence of ozonation on trihalomethane precursors at various pH's. THMFP conditions: pH as noted; temperature not given; storage time, 4 hr.[95]

lower TTHM concentrations than did chlorination of untreated water (Figures 78 and 79). On the other hand, the data in Table 40 (page 133) show that in some instances, higher concentrations of bromodichloromethane and dibromochloromethane were formed when the water was treated with chlorine dioxide. The reason for these results is unknown and may even be analytic error.

In the second phase of the Miltner study, two 5 mg/L humic acid mixtures were prepared.[39]* One sample was treated with 2 to 3 mg/L of laboratory-generated chlorine dioxide, and both samples were stored for 48 hours, during which time the chlorine dioxide in the treated sample was consumed. Both mixtures were then chlorinated. Again, chlorine dioxide was reacting to reduce the precursor concentration, as shown by the reduction in chloroform concentration (Figure 80, page 134). In this case, chloroform was the only trihalomethane produced. Although this work does demonstrate the ability of chlorine dioxide to alter precursor materials so that it does not participate in the trihalomethane formation reaction, as with ozone, the conditions used here are not typical of water treatment practice. The use of chlorine dioxide in a more typical manner will be reported in Section VIII.

Potassium Permanganate—A speculation by Rook[21] that the reaction of precursors to form trihalomethanes was characteristic of those of *m*-dihydroxyphenyl moieties led to some unpublished USEPA experiments on treatment of resorcinol and *m*-dihydroxybenzoic acid solutions with potassium permanganate at low dosages. As expected, this treatment was nearly 100 percent

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*The humic acid solution was made using 5 mg of humic acid (Aldrich Chemical Company) mixed in 1 liter of distilled water that had been passed through a Super-Q (Millipore Filter Co.) filter and redistilled in glass; the pH was then adjusted to 10. After mixing, this solution was adjusted to pH 7 and mixed for several hours.

TABLE 39. TRIHALOMETHANE PRECURSOR REDUCTION WITH OZONE[24,25]

Location	Ozone dose, mg/L	Percent TermTHM* reduction
Owens River	1.0	78
Lake Casitas	2.0	6
Columbia River	0.5	8
Columbia River	1.0	14
Columbia River	2.0	16
Columbia River	4.0	16
Ohio River (Louisville)	1.0	6
Ohio River (Louisville)	2.0	22
Ohio River (Louisville)	4.0	30
Ohio River (Louisville)	6.0	46
Ohio River (Louisville)	8.0	46
Bay Bull's Big Pond	1.0	13
Bay Bull's Big Pond	2.0	19
Bay Bull's Big Pond	3.0	27
Mokelumne Aqueduct No. 2	2.0	62
Mokelumne Aqueduct No. 2	3.4	59
Mokelumne Aqueduct No. 2	4.5	59
Mokelumne Aqueduct No. 2	6.0	53
Middle River	2.6	-13
Middle River	2.8	-3
Middle River	5.5	32
Middle River	10	7
Middle River	11	22
Rotterdam	2	60
Rotterdam	8	50
Orange County	1.0	7

*Measurement conditions not specified.

effective in preventing the formation of trihalomethanes upon later chlorination of these substances. To investigate whether or not treatment by potassium permanganate would remove trihalomethane precursors, Ohio River water was dosed with potassium permanganate, stored, and subsequently chlorinated. Chlorination in these experiments was carried out in the presence of the precipitated manganese dioxide as well as excess, unreacted potassium permanganate. Therefore, apparent lower precursor concentrations after treatment cannot be attributed to precipitation and therefore are likely to be the result of the oxidation process. Selected data from this experiment (Table 41, page 134) indicate limited success in removing trihalomethane precursors from Ohio River water. The results were variable, depending on conditions of both potassium permanganate and chlorine treatment. Note that when potassium permanganate treatment and chlorination are both carried out at high pH (experiment 2,3), the treatment for precursors does not appear to be as effective as when both are carried out at neutral pH (experiment 1,5). The overall yields of trihalomethanes are also greater at high pH (not shown). The reverse is true, however, when the chlorination pH is a constant 7.0 (experiment 1,6), showing that potassium permanganate is a better oxidant for precursor removal at high pH.

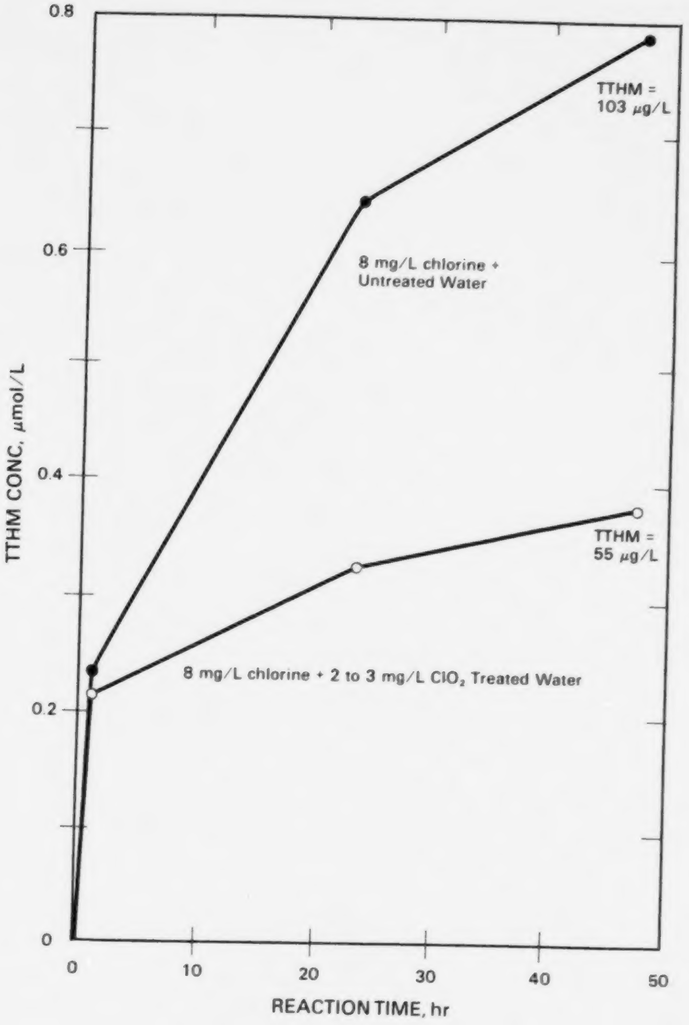

Figure 78. TTHM concentration after chlorination of chlorine dioxide treated and untreated Ohio River water, pH 7.6; 25°C (77°F).[39]

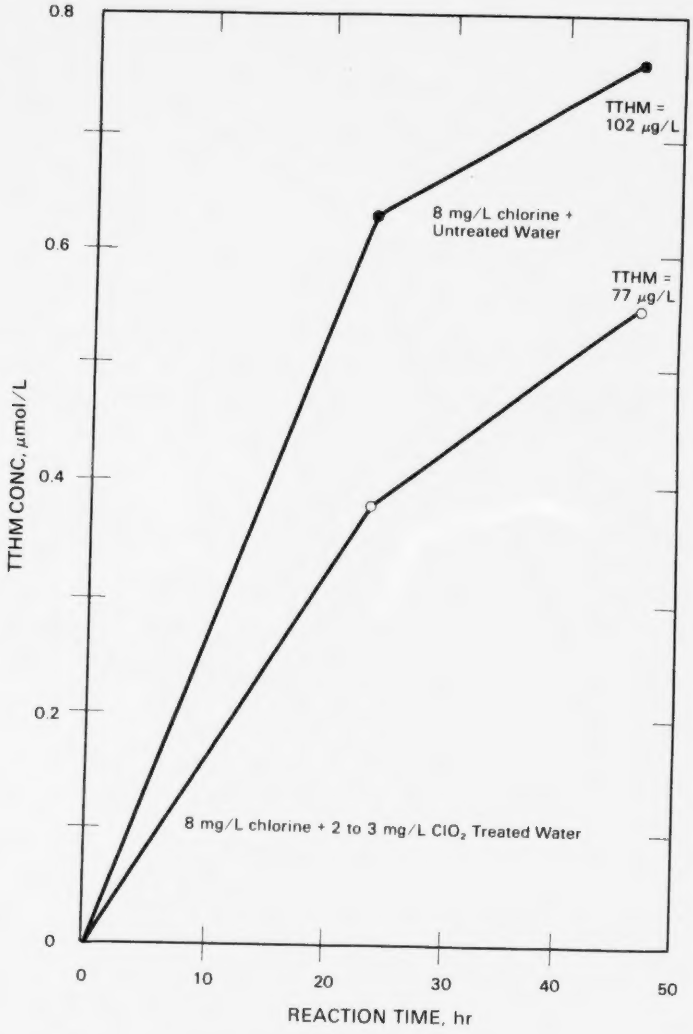

Figure 79. TTHM concentration after chlorination of chlorine dioxide treated and untreated Ohio River water, pH 6.8; 25°C (77°F).[39]

TABLE 40. EFFECT OF CHLORINE DIOXIDE ON TRIHALOMETHANE PRECURSOR CONCENTRATION IN OHIO RIVER WATER[39]

Type of water	Free chlorine, mg/L		Storage time, hours	Trihalomethanes, $\mu g/L$				Term TTHM,* $\mu mol/L$	Percent reduction TTHM
	Dose	Residual		$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$		
Raw water (control)	8	Yes†	24	59	18.5	4	NF‡	0.628	—
ClO_2^- treated water§	8	Yes	24	30	15	8	NF	0.382	39
Raw water (control)	8	3.9	47.5	76	21.6	4	<0.4	0.765	—
ClO_2^- treated water§	8	4.7	47.5	41	23	13	NF	0.547	29

*Temperature, 25°C (77°F); pH, 6.8, storage time as shown.
†Not quantified.
‡None found.
§2 mg/L ClO_2.

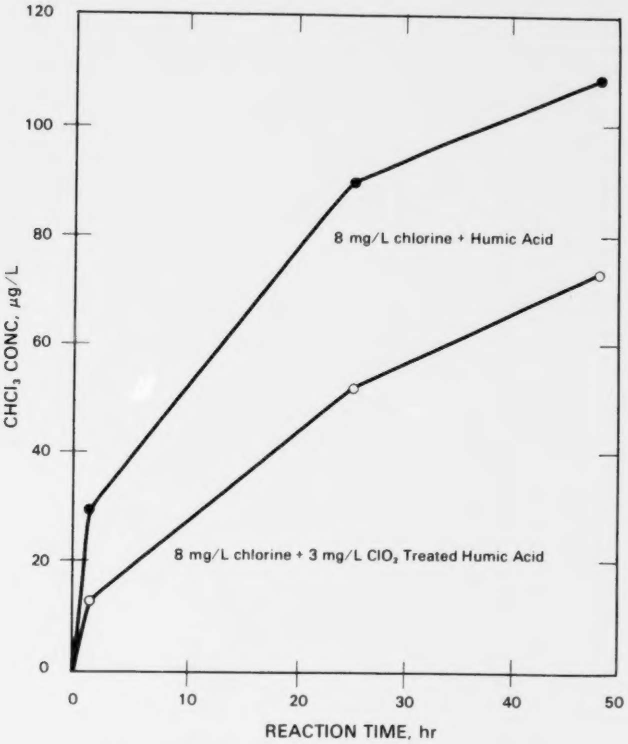

Figure 80. Chloroform concentration after chlorination of chlorine dioxide treated and untreated humic acid solutions. pH 7.0; 25°C (77°F).[36]

TABLE 41. TRIHALOMETHANE PRECURSOR REMOVAL BY POTASSIUM PERMANGANATE IN OHIO RIVER WATER

	KMnO$_4$ reaction			Chlorine reaction				
Experiment No.	Amount added, mg/L	Reaction time, hours	pH	Cl$_2$ added, mg/L	Total oxidant residual,* mg/L	Reaction time, hours	pH	Percent TermTTHM reduction
1	0	1.5	7.1	10.5	9.3	2	7.0	
	5	1.5	7.1	10.5	13.5	2	7.0	15.4
2	0	1.5	9.3	10.5	9.1	2	9.0	
	5	1.5	9.3	10.5	13.3	2	9.0	2.7
3	0	1.5	10.2	10.5	9.1	2	9.9	
	5	1.5	10.2	10.5	13.5	2	9.9	5.6
5	0	21	7.0	8.9	6.0	24	7.0	
	10	21	7.0	8.9	14.7	24	7.0	25.0
6	0	21	11.5	8.9	6.0	24	7.0	
	10	21	11.5	8.9	12.9	24	7.0	35.3

*Recorded as mg/L Cl$_2$ and includes excess unreacted KMnO$_4$ (where applicable) as well as chlorine.

Singer et al. conducted similar experiments using the raw water supplies of Chapel Hill and Durham, North Carolina.[97] Both are surface supplies with high THMFP. These experiments also demonstrated greater effectiveness of potassium permanganate treatment at high pH values when chlorination was carried out near neutrality. Removals of 30 to 40 percent were reported when potassium permanganate treatments of 10 mg/L were carried out at pH 6.5 and 10.3, respectively. Because these samples were filtered before chlorination, some of this removal is the result of precursor precipitation with manganese dioxide, although this effect was considered by the authors to be much less than that caused by the oxidation mechanism. In their conclusions, the authors state that potassium permanganate can decrease the chloroform formation potential of a water and that the extent of this decrease is related directly to the potassium permanganate dose. In addition, at the pretreatment doses of potassium permanganate normally employed (1.5 mg/L or less), the effect of this treatment is relatively small, and accordingly, if potassium permanganate is to be used specifically for this purpose, much larger doses will be required.

Ozone—Ultra-violet Radiation—To determine whether or not irradiating water with ultra-violet light while treating it with ozone (O_3/UV) would enhance the destruction of trihalomethane precursors, Glaze et al. treated a precursor-rich lake water with O_3/UV.[40] Although they did not examine ozone alone as a control in this study, their data (Figure 81) do show that at a constant ozone dose, a 4-fold increase in radiation intensity reduced the treatment time to reach 100 μg/L of THMFP (3-day, pH 6.5, 26°C [79°F]) from 40 to 21 minutes in the batch reactor. This result shows that increased quantities of UV energy enhance the removal of precursor when ozone is used.

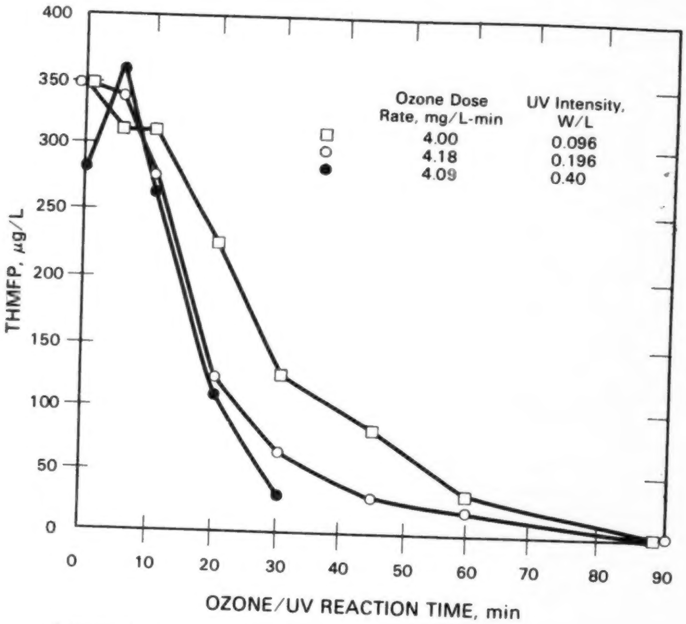

Figure 81. Destruction of trihalomethane precursors in Cross Lake, TX, water by O_3/UV. THMFP conditions; pH 6.5; 26°C (79°F); storage time, 3 days.[40]

Hydrogen Peroxide—Hydrogen peroxide has been suggested as an oxidant that could be used for the removal of trihalomethane precursors. This possibility has been briefly studied by two investigators,[98,99] but unfortunately, both used the unrealistic direct aqueous injection method[28] of estimating precursor concentrations (see Section IV). Conclusions on the usefulness of hydrogen peroxide for precursor oxidation therefore cannot be made.

Discussion—

Each of the oxidation techniques discussed in this subsection—ozone, chlorine dioxide, potassium permanganate, and ozone/ultra-violet radiation—had some effect on THMFP concentrations. Doses of the oxidants were higher and contact times longer, however, than normally used in disinfection practice to accomplish significant lowering of THMFP. Further, although the precursor materials were altered so that they no longer could participate in the trihalomethane formation reaction, these studies did not determine the exact fate of these materials. Thus, the possibility of creating undesirable byproducts from these oxidative reactions cannot be ruled out at this time. This means that batch and pilot studies will be required on a case-by-case basis to determine the ultimate applicability of oxidative techniques for lowering THMFP. Oxidation reactions of precursor materials are likely to be rather complex, and byproducts obtained will vary significantly with reaction conditions, as will removals of THMFP. Finally, waters high in bromide that produce high concentrations of TTHM *might* be treated with ozone to retard or prevent the formation of the bromine-containing trihalomethanes, thereby lowering the TTHM concentrations. More work will be needed to investigate this possibility.

Adsorption

Powdered Activated Carbon (PAC)—

General Considerations—Because trihalomethane precursors are a mixture of many organic chemicals, and this mixture varies from location to location, treating adsorption of these substances in a theoretical manner is much more difficult than treating the adsorption of the individually identifiable and quantifiable trihalomethanes. Aquatic humic materials, a major contributor to trihalomethane precursors, are not themselves a single substance. Unlike the individual trihalomethanes, the characters of these acidic materials are influenced by numerous variable factors that will influence their adsorbability. These factors include molecular weight distribution, pH, inorganic ions present, precursor source, and relative fractions of humic and fulvic acids.[89]

These variables are beyond the influence of the physical-chemical characteristics of the solution on the activated carbon surface itself (which, of course, will affect the adsorption of even pure substances). Also, trihalomethane precursors cannot be measured directly, but only by the resulting trihalomethanes formed upon chlorination of a test sample. Furthermore, the quantity of trihalomethanes formed depends on the test conditions selected, time of storage, temperature of storage, and storage pH. The mixture of trihalomethanes formed as well as their total quantity will depend on the bromide concentration in the water. Thus experimental adsorption results seemed likely to be quite variable, depending on the water being treated for precursor removal. Nevertheless, several studies have been conducted that attempt to demonstrate how the THMFP (in μmol/L) is lowered by treatment with various doses of PAC. These studies are reviewed here.

Experimental Results—An in-house USEPA study assessed the effectiveness of PAC on the removal of trihalomethane precursors from Ohio River water that had been coagulated and settled. This water was dosed with varying concentrations of PAC, mixed at 100 rpm for 2 minutes, and centrifuged for 20 minutes at 1,500 rpm (480 gravities). The supernatant liquor was then decanted and chlorinated. These samples were then stored for 2 days at 25°C (77°F) (pH was not recorded). Four studies were made with three brands of PAC. Extrapolation from the resulting adsorption isotherms from three of the studies (Figure 82) show that about 43 mg/L of PAC would be required to reduce the THMFP from 1 to 0.5 μmol/L in this water. The adsorption isotherm for the Watercarb® material is atypical and indicates that it would not be an effective adsorbent for trihalomethane precursors (Figure 82).

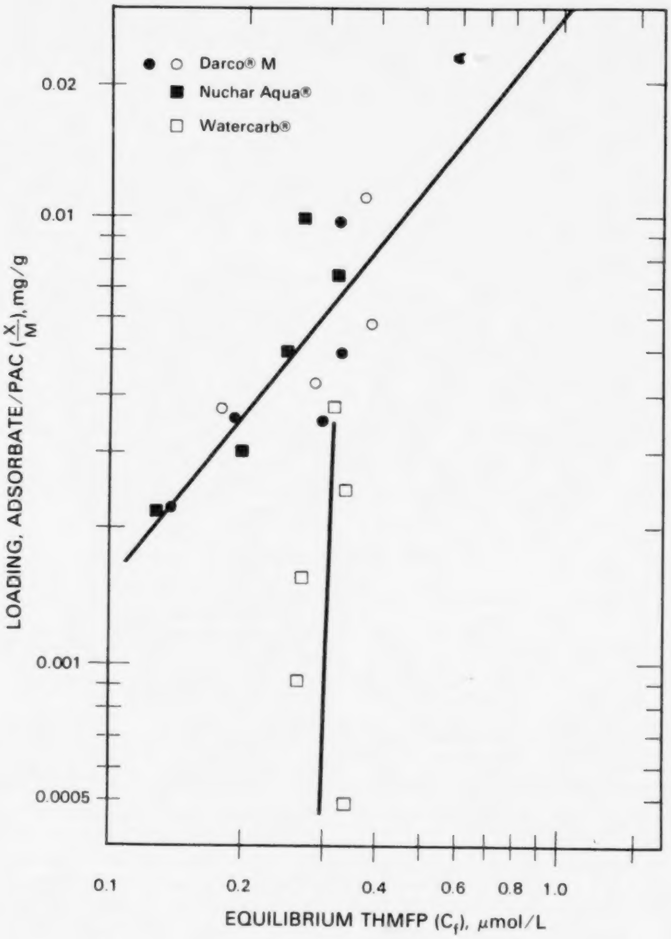

Figure 82. Adsorption isotherms from three studies using PAC to remove trihalomethane precursors from coagulated and settled Ohio River water. THMFP conditions: pH, not reported; 25°C (77°F); storage time, 2 days. (Darco® M manufactured by ICI America, Inc., Atlas Chemical Division, Wilmington, DE 19899; Nuchar Aqua® manufactured by Westvaco Corporation, Covington, VA 24426.)

A project at the New Orleans, LA, water utility was reported by Lykins and DeMarco.[100] The adsorption isotherm from these data for raw Mississippi River water (Figure 83) would indicate that about 77 mg/L of PAC would be required to reduce the THMFP concentration from 1 to 0.5 μmol/L.

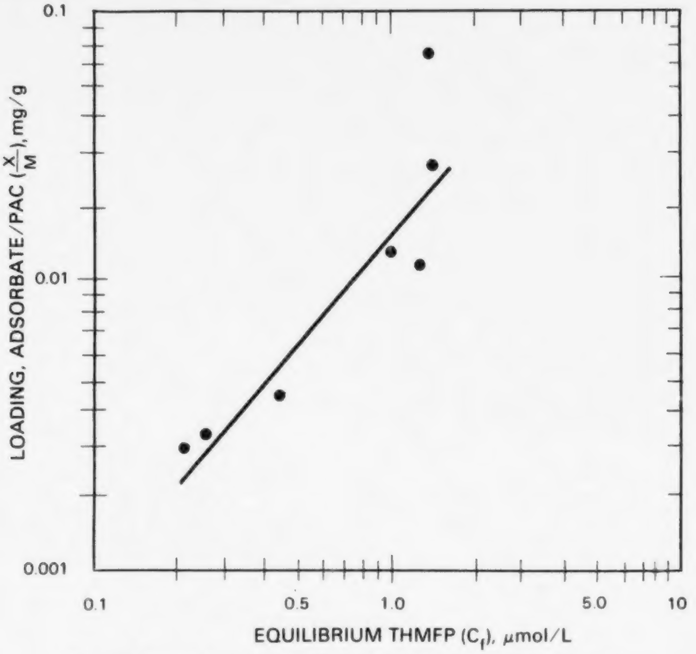

Figure 83. Adsorption isotherm from New Orleans, LA, study using PAC to remove trihalomethane precursors from Mississippi River water. THMFP conditions: pH 10; 29°C (85°F); storage time, 5 days.[100] (Hydrodarco® B manufactured by ICI America, Inc., Atlas Chemical Division, Wilmington, DE 19899.)

Other studies have been reported in the literature showing various degrees of effectiveness for the removal of trihalomethane precursors by PAC,[54,101] but the above two examples seem to illustrate a range of applicability of this technique.

Discussion—The results presented clearly indicate that the effectiveness of PAC at any given location will be subject to wide variability because of the factors outlined under General Considerations in this Section as well as the characteristics of the selected PAC itself. Case-by-case studies will be required to determine the actual effectiveness of this treatment technique. In general, doses of PAC much higher than conventionally used in existing water treatment practices seem to be required to obtain significant removals of trihalomethane precursors.

Granular Activated Carbon (GAC)—

General Considerations—Section VI included a discussion of factors influencing adsorption of pure materials (trihalomethanes) and a general description of the performance characteristics of a typical dynamic adsorption system compared with those of a theoretical plug flow system in which simple equilibrium calculations can be used to estimate times to "exhaustion." The data that followed in that section indicated that equilibrium calculations based on PAC isotherms were of marginal utility in predicting performance of the GAC systems studied. Kinetic effects, influencing the shape of the mass transfer zone, and other factors were important in causing significant deviations between column performance predicted solely from isotherm data and actual experimental results. This was the case even when the targets of treatment were well-known and reproducible experiments could be conducted.

As discussed above for PAC adsorption of precursors, many more factors influence the results of adsorption experiments involving trihalomethane precursors. Although isotherm data may prove to be useful to determine the *feasibility* of using GAC adsorption for the removal of precursors under a given set of circumstances, little is to be gained by attempting to estimate adsorber life in a general sense because of the variables between systems.

Furthermore, as will be seen below, GAC adsorbers do not typically reach "exhaustion" at all. The equilibrium state (influent equals effluent concentration) rarely occurs in practice, and a "steady state" condition prevails over a long period of time. Under this condition, the effluent concentration of THMFP remains significantly below that of the influent. This is usually considered to be the result of biologic activity within the bed, although other explanations have been proposed.[102]

Therefore, because of these general considerations, no attempt will be made to predict dynamic GAC adsorber performance from a given set of equilibrium (isotherm) data. The following is a compilation of experimental results from pilot and field studies that will be used to develop a general picture of the effectiveness of the GAC adsorption technique for removal of precursors.

Experimental Results—For the in-house USEPA studies, a pilot water treatment plant was fabricated to provide a continuous supply of treated but unchlorinated water for trihalomethane precursor removal studies. To minimize contamination from structural materials, the pilot plant was built almost entirely of stainless steel, Teflon®, and glass, and it was housed in a room kept free from organic contamination in the air. Through the assistance and cooperation of the Cincinnati Water Works, Ohio River water was provided as a source of raw water. The pilot plant employed conventional alum coagulation, flocculation, and sedimentation; the unchlorinated settled water was pumped through GAC adsorbers fabricated with glass columns 3.7-cm (1.5-in) in diameter. For this study, two depths of GAC were used: A 76-cm (30-in) deep bed of coal-based GAC and a 150-cm (60-in) deep bed of lignite-based GAC. The THMFP was evaluated by chlorinating influent and effluent samples from the adsorber and comparing the resulting trihalomethane concentrations.

The results from the 76-cm (30-in) deep coal-based GAC system with a 9-minute EBCT (Figure 84) show three important points: (1) when fresh, this GAC adsorbed nearly all of the trihalomethane precursors from this water, as shown by the low concentrations of trihalomethanes formed when the fresh GAC effluent was chlorinated; (2) some trihalomethane precursor began to pass the adsorber almost immediately, as shown by the steady rise in the concentration of trihalomethanes produced upon chlorination of the GAC effluent; and (3) because of the faster reaction between bromine and precursor compared with chlorine and precursor, the bromine-containing trihalomethanes will be formed first (if bromide is present in the water) as the trihalomethane precursor begins to break through a GAC adsorber and the effluent is chlorinated.

For example, in Figure 84, the concentration of dibromochloromethane in the chlorinated effluent sample equalled the concentration in a chlorinated influent sample at 4 weeks, whereas the concentration of bromodichloromethane in the chlorinated effluent sample did not equal the concentration in a chlorinated influent sample until the 8th week. Furthermore, the concentration of chloroform in the chlorinated adsorber effluent sample did not equal the concentration in a chlorinated influent sample until the 13th week. Thus, the first precursor to penetrate

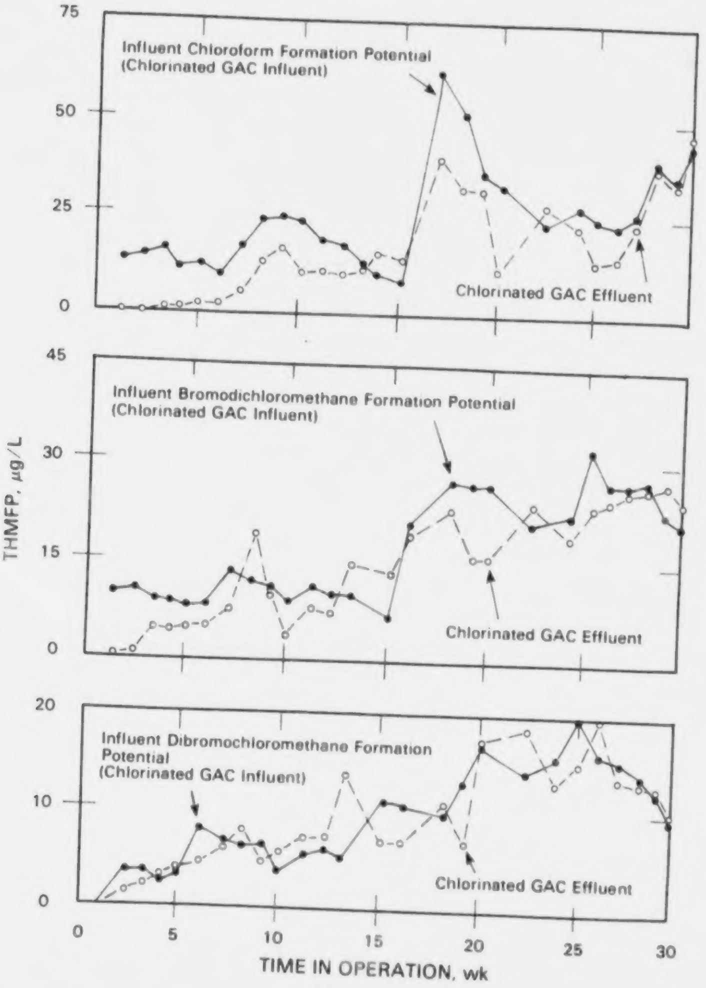

Figure 84. Removal of trihalomethane precursors from Ohio River water by coal-base GAC. Test period, March-October 1975; GAC type, Filtrasorb® 200; bed depth, 76 cm (30 in); hydraulic loading, 5 m/hr (2 gpm/ft^2); EBCT, 9 min. THMFP conditions: pH 6.5; 20°C (68°F); storage time, 4 days.

the adsorption system reacted with the active bromine species to form dibromochloromethane. Apparently insufficient bromide was present to cause formation of the pure-halogen trihalomethane, $CHBr_3$.

These data would indicate that for this adsorbent, exhaustion for precursor removal occurred about the 13th week in this system with a 9-minute EBCT. The influent to this system contained approximately 0.28 μmol/L of THMFP.

The data for the deeper lignite-based GAC adsorber with an 18-minute EBCT (Figure 85) show the same results as noted above—good precursor removal at first, bromine-containing trihalomethanes being formed as precursor materials begin to break through, and a fairly rapid breakthrough of precursor. These data do show one important difference, however. In this case, some removal of trihalomethane precursor was taking place even after 30 weeks of operation. This effect is shown particularly by the difference in the concentrations of influent chloroform formation potential and the chloroform formed upon chlorination of the adsorber effluent.

The service time to exhaustion of the bed with an 18-minute EBCT might be expected to be twice as long as that with 9 minutes even though different sources of granular activated carbon were used, but removals continued much longer than expected in the deeper bed. Although the GAC source is one explanation for this, biodegradation of precursor within the bed is also considered to be a factor.

A Huntington, WV, project[18] and a Jefferson Parish, LA, study[14] confirmed the results obtained in the pilot plant studies—good removal of trihalomethane precursors early in the test, fairly rapid breakthrough of precursor materials, and lack of true exhaustion, possibly because of biologic activity (Figures 86 and 87). These two sets of data also show the predicted general relationship between EBCT and time to reach steady-state operations (defined as the service time when the percentage of trihalomethane precursor being removed is no longer declining). For the Huntington, WV, system, this condition was reached at about 6 weeks for an EBCT of 7.1 minutes; whereas for the Jefferson Parish study, the time to reach steady-state conditions was about 20 weeks for a 23-minute EBCT. Table 42 (page 145) summarizes the data from the USEPA projects and from selected literature citations on the performance of GAC adsorption as a unit process for removing trihalomethane precursor. These data are ranked in ascending EBCT order to show as far as possible the influence of longer EBCT's on the rate of trihalomethane breakthrough and the percent of precursor removed during steady-state operation. Influent THMFP and sample storage conditions for the THMFP test are given to assist the reader in selecting examples of treatment conditions most appropriate for comparison with a particular utility.

With the data of Wood and DeMarco from Miami, FL,[87] a bed-depth service time plot[68] was constructed for the removal of trihalomethane precursors at that location (Figure 88, page 148). These data show that the minimum adsorber bed depth is 19 cm (7.5 in) to remove THMFP to 200 μg/L and 32 cm (12.5 in) to reach 100 μg/L from an average influent concentration of 434 μg/L. Of course, if a lower target were chosen, the minimum bed depth would be correspondingly greater. Note that because trihalomethane precursors are a mixture of compounds, they do not behave as pure substances behave. For example, using additional data from this study, the bed-depth service time plots for target concentrations of 50 and 20 μg/L were nonlinear, but they did indicate a thicker critical depth. This approach to adsorber design may have only limited application here.

Discussion—The data in Table 42 confirm the generalized conclusions drawn from Figures 84 through 87: (1) GAC adsorption is initially very effective for trihalomethane precursor removal; (2) in practice, the rate of trihalomethane precursor breakthrough is fairly high; and (3) exhaustion (defined as an effluent concentration equal to influent concentration) usually does not occur, but rather a steady-state develops during which a rather constant percentage of precursor material continues to be removed, possibly because of biodegradation.

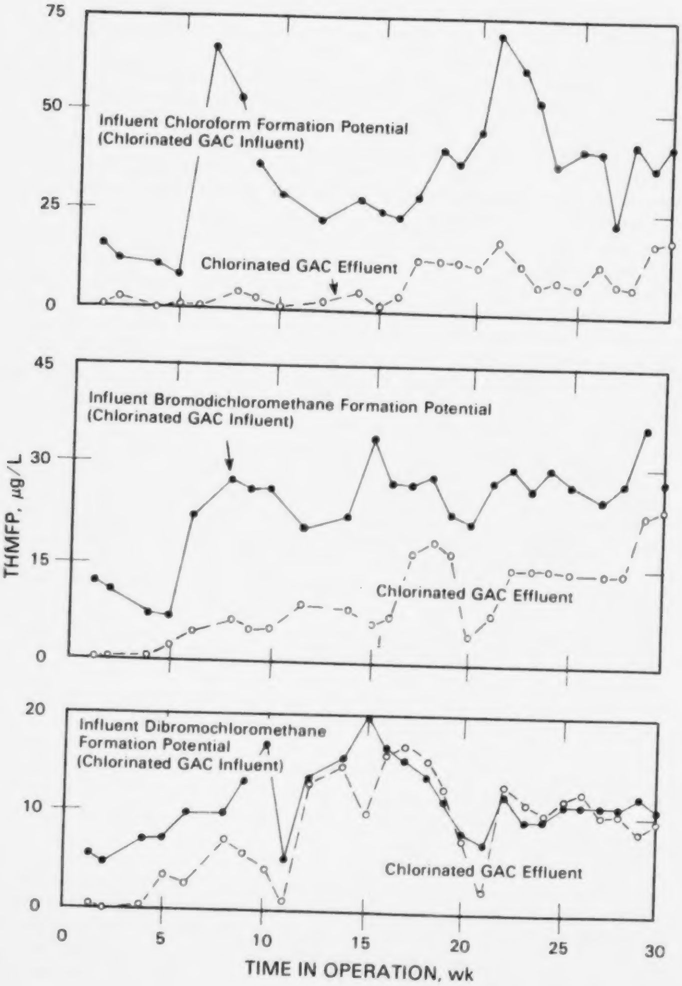

Figure 85. Removal of THMFP from Ohio River water by lignite-base GAC. Test period, May–December 1975; GAC type, HD 10 × 30; bed depth, 152 cm (62 in); hydraulic loading, 5 m/hr (2 gpm/ft²); EBCT, 18 min. THMFP conditions: pH 6.5; 20°C (68°F); storage time, 4 days.

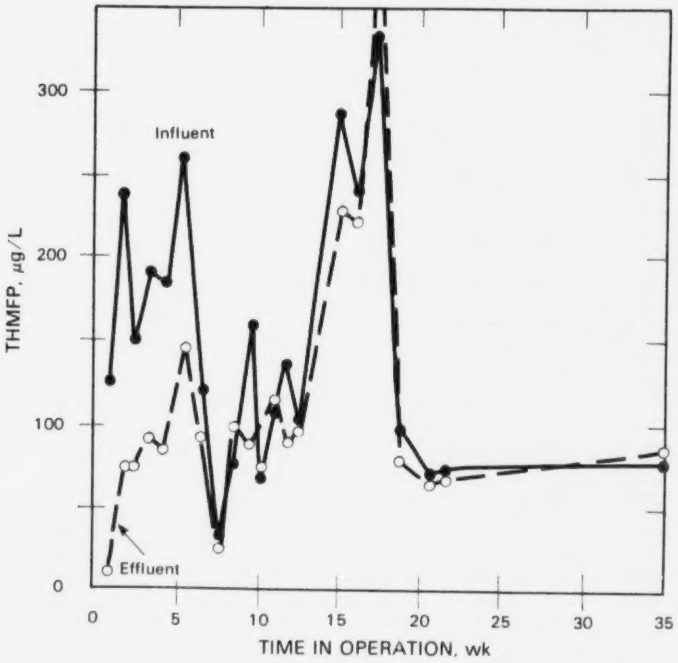

Figure 86. Removal of trihalomethane precursors by GAC at the Huntington Water Corp. (WV). GAC type, WVW 14 × 40; bed depth, 76 cm (30 in); hydraulic loading, 6.1 m/hr (2.6 gpm/ft²); EBCT, 7.1 min. THMFP conditions: pH 8.3; ambient temperature; storage time, 7 days.[18]

Although the data (Table 42) are quite scattered, because of being collected in different locations and because of different sample storage conditions for THMFP measurement, adsorbers with longer EBCT's removed precursor longer and demonstrated a higher percentage removal at steady state conditions. Because of the variability of waters being treated and the necessity of varying THMFP test conditions to approximate reaction conditions experienced at a given utility, drawing more concise conclusions is difficult. Thus, continuous flow pilot studies must be performed at each location to determine the breakthrough patterns and potential long-term removals at steady state to be expected in practice. Finally, as trihalomethane precursor materials begin to break through a GAC adsorber, if bromide is present, the bromine-containing trihalomethanes appear first upon chlorination because of the rapid oxidation of bromide by chlorine to an active bromine species that then reacts quickly with whatever precursor material is present (Figure 84).

Synthetic Resins—

General Considerations—Ambersorb® XE-340, which was shown to be effective for trihalomethane removal (Section VI, Subsection, Synthetic Resins) was evaluated to determine whether or not it could also effectively adsorb trihalomethane precursors.

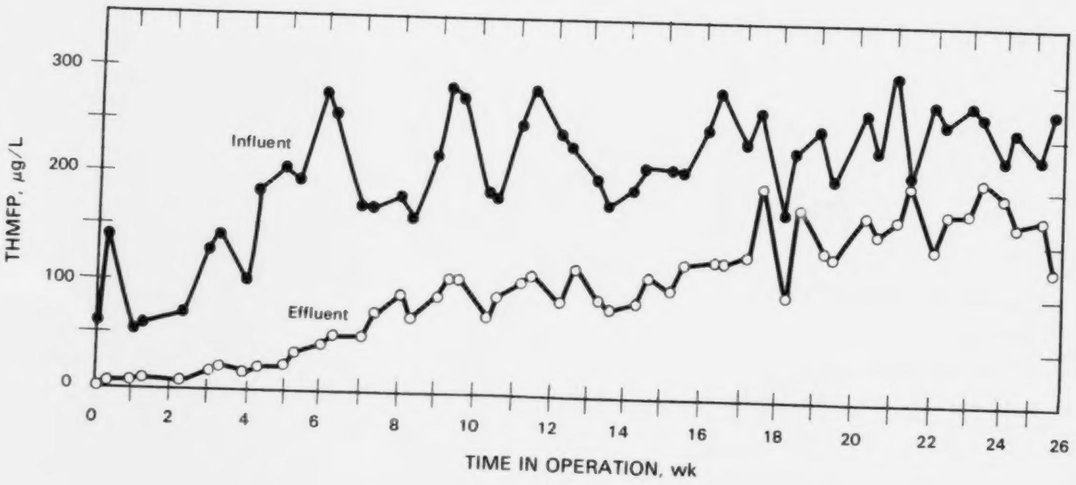

Figure 87. Removal of trihalomethane precursors by post filter GAC adsorber, Jefferson Parish, LA. GAC type, WVG 12 × 40; bed depth, 71 cm (28 in); hydraulic loading, 1.9 m/hr (0.75 gpm/ft^2); EBCT, 23 min. THMFP conditions: pH 10; 21°C (70°F); storage time, 5 days.[14]

TABLE 42. SUMMARY OF PERFORMANCE DATA FOR REMOVAL OF TRIHALOMETHANE PRECURSORS BY VIRGIN GAC ADSORPTION

Location	Type of GAC	Type of system*	EBCT, min	Approximate percent initial THMFP removal	Approximate time to steady-state conditions,† weeks	Percent THMFP removal at steady-state conditions	Influent THMFP at steady-state conditions, μg/L	Sample storage conditions Time, days	Temperature, °C§§	pH	Reference
Cincinnati, OH	WVG 12x30	PC/PF	3.2	97	4	6	281	7	29.4	9.2	30
Cincinnati, OH	HD 10x30	PC/PF	3.2	97	2	14	232	7	29.4	9.2	30
Evansville, IN	HD 10x30	PC/PA	3.7	84	6	16	58	3	17	8.0	63
Cincinnati, OH	WVG 12x40	FS/SR	4.5	95	2	38	222	7	29.4	9.2	30, 62
Mt. Clemens, MI	HD 3000‡	FS/SR	5.8	81	4	32	51	5	25	7.3	NR§
Mt. Clemens, MI	HD 3000‡	FS/SR	5.8	75	4	32	60	5	25	7.3	NR
Evansville, IN	HD 10x30	PC/PA	6.6	87	6	26	58	3	17	8.0	63
Huntington, WV	WVW 14x40	FS/SR	7.1	93	6	11	120	7	20	8.3	18
Davenport, IA	Filtrasorb® 400	FS/SR	7.5	UNK**	>14	73	26	**	**	**	66
Cincinnati, OH	WVG 12x40	FS/SR	7.5	97	2	50	222	7	29.4	9.2	30, 62
Cincinnati, OH	WVG 20x50	FS/SR	7.5	97	2	33	222	7	29.4	9.2	30, 62
Cincinnati, OH	WVG 12x40	PC/PF	7.5	98	4	41	281	7	29.4	9.2	30
Cincinnati, OH	HD 10x30	PC/PF	7.5	**	4	30	281	7	29.4	9.2	30
Cincinnati, OH	Filtrasorb® 200	PC/SR	9.0	97	16	0	27	4	20	6.5	††
Cincinnati, OH	Filtrasorb® 400	PC/SR	9.0	88	16	40	42	2	50	**	††
Cincinnati, OH	WVG 12x40	PC/SR	9.4	95	6	37	244	7	29.4	9.2	30
Cincinnati, OH	WVG 12x40	PC/SR	9.4	93	6	36	244	7	29.4	9.2	30
Evansville, IN	HD 10x30	PC/PA	9.6	89	6	31	58	3	17	8.0	63
Cincinnati, OH	Filtrasorb® 400	PC/PA	10.0	93	16	44	137	6	25	7.8	††
Beaver Falls, PA	Filtrasorb® C‡‡	FS/SR	10.1	**	11	11	110	7	10-20	7.4	18

Continued

TABLE 42. (Continued)

Location	Type of GAC	Type of system*	EBCT, min	Approximate percent initial THMFP removal	Approximate time to steady-state conditions,† weeks	Percent THMFP removal at steady-state conditions	Influent THMFP at steady-state conditions, μg/L	Sample storage conditions			
								Time, days	Temperature, °C§§	pH	Reference
Jefferson Parish, LA	WVG 12x40	PC/PA	11.0	68	18	0	251	5	30	10	14
Beaver Falls, PA	Filtrasorb® 400	FS/SR	11.3	**	11	19	110	7	10-20	7.4	18
Beaver Falls, PA	HD 8x16‡	FS/SR	11.4	**	11	15	110	7	10-20	7.4	18
Cincinnati, OH	WVG 12x40	PC/PF	11.8	98	8	40	230	7	29.4	9.2	30
Cincinnati, OH	HD 10x30	PC/PF	11.8	97	4	34	281	7	29.4	9.2	30
Jefferson Parish, LA	Filtrasorb® 400	PC/PA	12.0	77	20	17	273	5	30	10	14
Jefferson Parish, LA	WVG 12x40	FS/SR	14.0	64	8	21	281	5	30	10	14
Jefferson Parish, LA	WVG 12x40	FS/SR	14.0	74	18	11	319	5	30	10	14
Cincinnati, OH	WVG 12x40	PC/PA	16.0	98	8	60	230	7	29.4	9.2	30
Cincinnati, OH	HD 10x30	PC/PA	16.0	97	5	35	259	7	29.4	9.2	30
Jefferson Parish, LA	WVG 12x40	PC/SR	17.0	10	18	13	319	5	30	10	14
Jefferson Parish, LA	WVG 12x40	FS/PA	18.0	65	21	14	192	5	30	10	14
Cincinnati, OH	HD 10x30	PC/SR	18.0	92	23	49	73	4	20	6.5	††
Jefferson Parish, LA	Filtrasorb® 400	FS/PA	19.0	53	21	25	365	5	30	10	14
Manchester, NH	WVW 8x30	FS/PA	21.7	78	8	52	138	7	28.5	8.0	103
Manchester, NH	WVW 8x30	FS/PA	21.7	82	8	47	133	3	28.5	8.0	103
Jefferson Parish, LA	WVG 12x40	PC/PA	22.0	18	22	20	235	5	30	10	14
Jefferson Parish, LA	Filtrasorb® 400	PC/SR	22.0	82	19	44	343	5	30	10	14
Jefferson Parish, LA	Filtrasorb® 400	PC/PA	23.0	69	21	39	365	5	30	10	14
Jefferson Parish, LA	WVG 12x40	PC/PA	23.0	55	21	20	192	5	30	10	14

Continued

TABLE 42. (Continued)

Location	Type of GAC	Type of system*	EBCT, min	Approximate percent initial THMFP removal	Approximate time to steady-state conditions,† weeks	Percent THMFP removal at steady-state conditions	Influent THMFP at steady-state conditions, μg/L	Sample storage conditions: Time, days	Sample storage conditions: Temperature, °C§§	Sample storage conditions: pH	Reference
Jefferson Parish, LA	Filtrasorb® 400	FS/SR	23.0	73	24	32	317	5	30	10	14
Jefferson Parish, LA	Filtrasorb® 400	PC/PA	23.0	81	21	34	365	5	30	10	14
Jefferson Parish, LA	WVG 12x40	FS/PA	24.0	90	20	32	265	5	30	10	14
Jefferson Parish, LA	WVG 12x40	PC/PA	33.0	58	24	28	149	5	30	10	14
Jefferson Parish, LA	Filtrasorb® 400	PC/PA	35.0	81	21	45	365	5	30	10	14
Jefferson Parish, LA	WVG 12x40	PC/PA	44.0	56	11	61	137	5	30	10	14
Jefferson Parish, LA	Filtrasorb® 400	PC/PA	46.0	88	17	69	253	5	30	10	14

*SR = sand replacement; FS = full scale; PA = post-filter adsorber; PC = pilot column.

†Percentage of THMFP being removed is no longer declining.

‡Manufactured by ICI America Inc., Atlas Chemical Division, Wilmington, DE 19899.

§Not reported.

**Unknown.

††In-house.

‡‡Not commercially available.

§§°F = °C × 1.8 + 32.

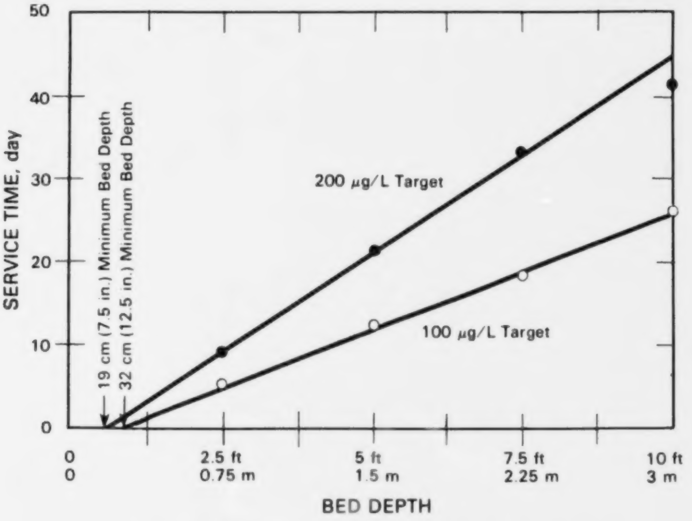

Figure 88. Bed depth-service times[58] for trihalomethane precursor adsorption by GAC. THMFP conditions: pH 9.0; 22°C (72°F); storage time, 6 days.[87]

Experimental Results—Ambersorb® XE-340 was tested in Miami, FL, for its ability to adsorb trihalomethane precursors.[104] In this case, two adsorbers with equal EBCT's (6.2 minutes) were compared—one treating source water, and the other treating lime-softened and filtered water. The data in Figure 89 show that Ambersorb® XE-340 is partially effective for the removal of THMFP from source water, but when treating water that had been pretreated by softening, the resin could no longer remove any precursor material.

Discussion—In this case, the type of precursor material that was adsorbable on Ambersorb® XE-340 also appeared amenable to removal by coagulation and sedimentation, and the precursor materials that remained following lime softening were not adsorbed on Ambersorb® XE-340. The generality of these observations has yet to be demonstrated, however.

Ion Exchange

General Considerations—

Because synthetic resins designed for other purposes are often reported to become fouled with organic contaminants while in service (Reference 105 as one example), they have been examined as possible trihalomethane precursor adsorbents. Also, because humic acids are anionic (particularly as the water becomes more alkaline), anion exchange resins were considered as good candidates for the removal of trihalomethane precursors.

Experimental Results—

Strong-Base Anion Exchange Resins—Amberlite® IRA-904—A synthetic resin manufactured by the Rohm & Haas Company, Philadelphia, PA 19105, is Amberlite® IRA-904. This material, a strong-base anion exchange resin, is used as an organic scavenger in some industrial processes. This resin was evaluated at Miami, FL.[104] Amberlite® IRA-904 was initially quite effective for removing

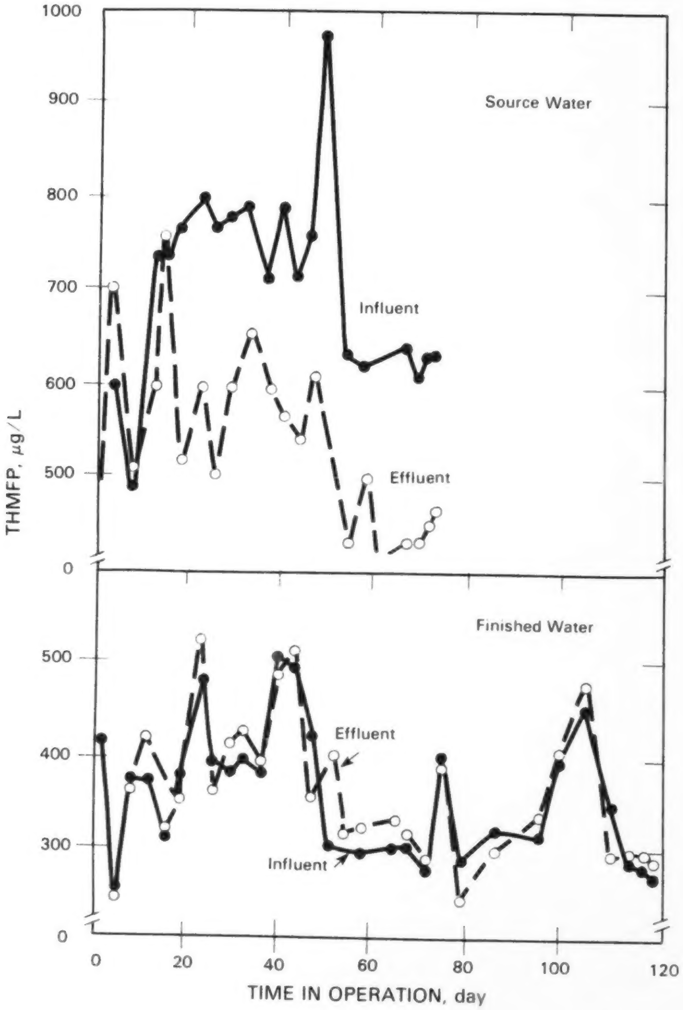

Figure 89. Removal of trihalomethane precursors by Ambersorb® XE-340; EBCT, 6.1 min. THMFP conditions: pH 9.0; 22°C (72°F); storage time, 6 days.[104]

trihalomethane precursor materials in the source water (as measured by THMFP), but it was unable to remove any precursor material from water that had been pretreated by lime softening (Figure 90). Either the residual precursor could not be exchanged or the high pH had an adverse influence on the resin itself. The unexchangeable fraction of precursor material also existed in the source water, as the initial contactor effluent concentration for THMFP (Figure 90) was the same even when the bed depth was doubled from 75 to 150 cm (30 to 60 in), with 9- and 18-minute EBCT's, respectively.

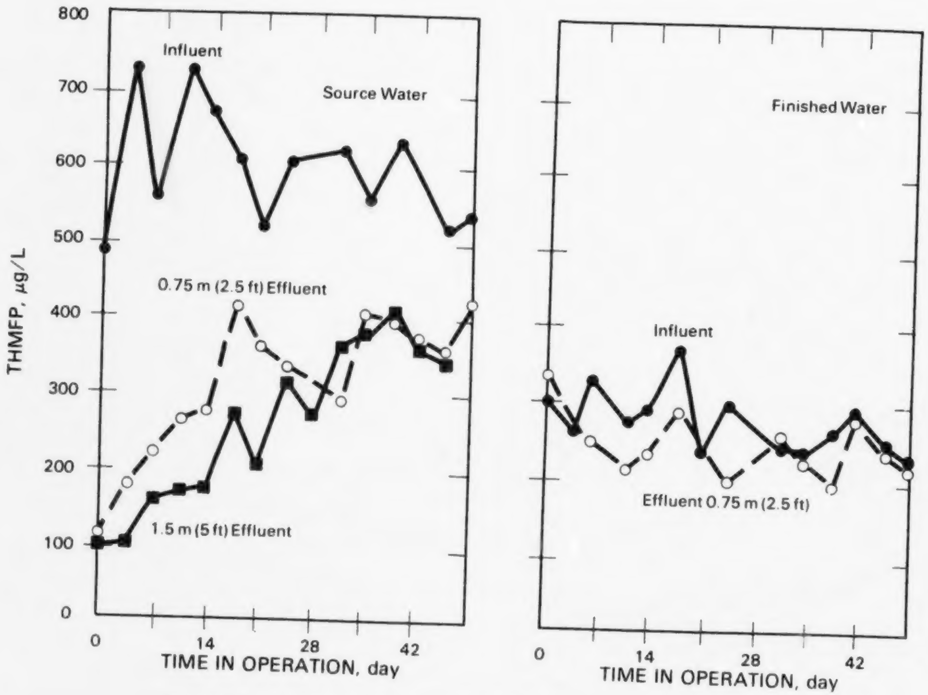

Figure 90. Removal of trihalomethane precursors by Amberlite® IRA-904; EBCT, 6.1, 12.2 min. THMFP conditions: pH 9.0; 22°C (72°F); storage time, 6 days.[104]

Asmit A259—A strong-base anion exchange resin manufactured by AKZO/Imacti Div., Amsterdam, The Netherlands, was evaluated at the Rotterdam Waterworks by Rook.[26] His results (Table 43) show some promise, although he stated that regeneration was necessary after 250 bed volumes of water were treated (the equivalent of less than 1 week of operation under normal circumstances). If regeneration were simple and inexpensive, this factor might not be a detriment.

TABLE 43. USE OF ASMIT A259 FOR REMOVAL OF TRIHALOMETHANE PRECURSORS* [26]

Sample	Trihalomethane formed, μg/L				TTHM formed, μg/L
	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	
Resin influent	28	13	8	6	55
Resin effluent	9	5	Trace	NF†	14

*Formation of trihalomethanes after 2 hours at 12°C (54°F) and pH 7.5-7.9.
†None found.

Weak-Base Anion Exchange Resins—Recently, Rook and Evans studied two weak-base anion exchange resins—A 20S, AKZO/Imacti Div., Amsterdam, The Netherlands, and 368 PR Duolite®, manufactured by Diamond Shamrock.[106] Two columns with an EBCT of 5.1 minutes were used to treat Meuse River water after sedimentation in a Lamella separator and dual-media filtration. Several tests were made, and Table 44 summarizes the results from the three runs in which the most water was treated. Significant removal rates were shown for both resins. Note that these resins are regenerated with lime followed by hydrochloric acid. Also, note that as with GAC adsorption (see preceding Subsection Granular Activated Carbon), the formation of the bromine-containing trihalomethanes is retarded the least during treatment for trihalomethane precursor removal. Again, an economic analysis would show whether or not these short runs are economical.

TABLE 44. USE OF WEAK-BASE ANION EXCHANGE RESINS FOR REMOVAL OF TRIHALOMETHANE PRECURSORS* [106]

Resin	Bed volumes treated	Inst. TTHM, μg/L	Percent precursor removal			
			$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	TTHM†
A 20S‡	1320	92	71	38	13	58
368 PR§	1320	92	77	50	7	64
A 20S	1250	71	86	46	17	66
368 PR	1250	71	86	58	17	69
A 20S	1780	57	64	40	9	48
368 PR	1780	57	68	45	9	52

*24-hr storage, 20°C (68°F), pH 7.5 to 8.0
†Molar sum.
‡A 20S AKZO/Imacti Div., Amsterdam, The Netherlands.
§368 PR Duolite®, Diamond Shamrock.

Discussion—

Of the anion exchange resins investigated, the weak-base resins studied by Rook and Evans[106] were the most effective. With these resins, however, the maximum length of the tests was only 6.3 days, and the disposal of the regenerate (lime and hydrochloric acid) may be a problem.

Biologic Degradation

General Considerations—

The data summarized in Table 42 show that steady-state conditions (during which a rather constant removal of trihalomethane precursors occurs) develop in GAC adsorption beds after some time of operation. One explanation for this effect is biologic degradation, in which the microorganisms are using the precursor materials—either adsorbed on the activated carbon surface or in the passing water—as a substrate. Several reports have indicated that preceding an adsorption step in a drinking water treatment train with ozonation (supposedly to fracture some organic molecules to make them more biodegradable) will improve the performance of the combination of the two processes over the performance of adsorption alone, presumably by enhancing the biologic degradation.[107,108,109] Results showing both the presumed naturally occurring biologic degradation as well as enhancement by the addition of ozone are presented here.

Experimental Results—

For the in-house USEPA studies to investigate this possibility, a 290-L/day (75 gpd) pilot column system was set up to treat unchlorinated coagulated and settled Ohio River water. Two 9-minute EBCT parallel columns were used; in one, settled water was applied directly to a GAC bed, and in the other, an oxygen plus ozone* mixture was added to the water before the filter/adsorber so that the ozone dose was approximately 1.5 to 2.5 mg/L. The GAC-only system reached steady-state conditions after 4 months (Figure 91), showing presumed natural biologic activity. For each of the 10 months studied, the monthly average THMFP in the effluent of the system with oxygen plus ozone treatment was always lower than the control system without oxygen plus ozone. This additional beneficial effect was presumed to be caused by enhanced biologic activity.

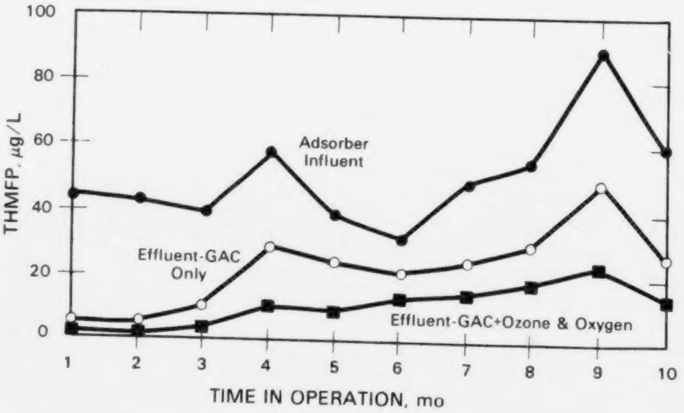

Figure 91. Influence of ozonation before adsorption on removal of trihalomethane precursors. THMFP conditions: pH, not reported; 25°C (77°F); storage time, 2 days.[36,104]

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*Because pure oxygen gas was used to generate the ozone, the gas fed into the gas contactor was an oxygen-ozone mixture. For accuracy, therefore, the term "oxygen plus ozone" is used for the system with oxidant added.

These findings led to a second experiment in which coagulated and settled Ohio River water (580 L/day or 150 gpd) was fed to two parallel treatment trains constructed of stainless steel, Teflon®, and 3.7-cm (1.5-in) diameter glass columns.[104] Each treatment train consisted of a gas contactor, a dual-media (anthracite coal over sand) filter, and a GAC column with a 10-minute EBCT. The gas contactor was an unpacked countercurrent-flow glass column with a stainless steel diffuser; the contact time was 18 minutes. One treatment train received untreated settled water as a control, and the test system received water that had been treated with oxygen plus ozone (the ozone dose was approximately 5 mg/L).

Investigations were carried out on the performance of this pilot column system for the removal of trihalomethane precursors. Data in Figure 92 show that the control was still removing 50 percent of the THMFP after 140 days of operation. This effect was possibly caused by naturally occurring biologic degradation. Furthermore, the data show that when oxygen plus 5 mg/L of ozone was added to the system as an additional treatment, the net effect was beneficial through the gas contactor, the dual-media filter, and the GAC adsorber. The effluent from that system had a consistently lower fraction remaining (C_e/C_i) of THMFP than did the control. This result confirms the data from the previous experience (Figure 91).

To investigate which unit process was responsible for the improved performance, the THMFP fraction remaining in the effluent of each of the unit processes, the gas contactor, the dual-media filter, and the GAC adsorber was compared individually with its respective control (Figure 92). Oxygen plus 5 mg/L ozone itself had some influence on the THMFP, as shown by a lower fraction remaining in the gas contactor effluent as compared with the control (Figure 92). This result is as expected (see earlier Subsection Oxidation).

Data in Figure 92 show that THMFP was being removed in the dual-media filter during the latter portion of the test, presumably because of biologic activity. Finally, little difference was shown in the performance of the GAC adsorber, in spite of the addition of oxygen plus 5 mg/L of ozone. THMFP removal was the same in the control GAC adsorber as in the test system.

In an effort to determine whether or not the expected biologic growths could be contained in the filtration/adsorption system, standard plate counts were determined for the influent settled water and for samples taken at each intermediate point in the treatment train. For the summer (from the start of the experiment through September 21, 1978), these data show that 5 mg/L of ozone reduced the geometric mean SPC from 2,900/mL in settled water to 16/mL in the gas contactor effluent (Figure 93); essentially no change occurred in the control.

Following the dual-media filter, however, the geometric mean standard plate count had rebounded to 26,000/mL in the system receiving oxygenated and ozonated water, whereas the geometric mean standard plate count actually declined somewhat through the dual-media filter of the control (Figure 93). This high bacterial population supports the contention that the organic removal occurring in the dual-media filter portion of the system was caused by biodegradation. Finally, measurement of the dissolved carbon dioxide content in the dual-media filter usually showed a higher concentration in the oxygen-plus-5-mg/L-ozone system than in the control—further evidence of biologic activity.

Discussion—

Evidence in these two pilot-scale experiments indicates that biologic activity is presumed to occur naturally in GAC adsorbers and that this activity can be enhanced by the use of ozone as an additional treatment. Furthermore, a highly active adsorbing media does not seem to be required, as shown by the removal of trihalomethane precursors that occurred in the dual-media filter during the second experiment described above. Biologic degradation of precursor materials seems to be the only logical explanation of removal on the dual-media filter. Research is under way with other oxidants and longer EBCT inert media systems[110,111,112] to

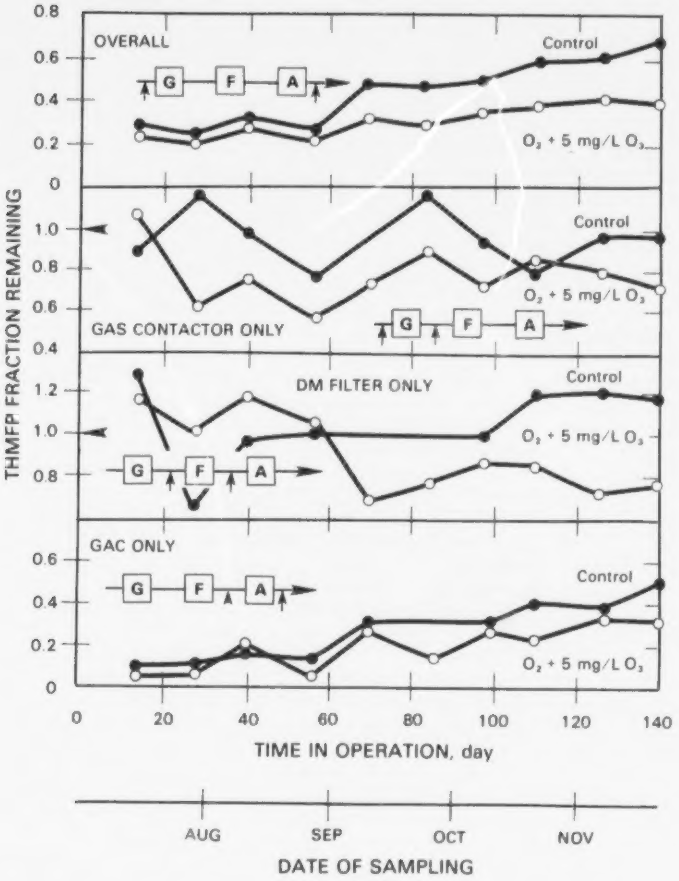

Figure 92. Removal of trihalomethane precursors by various steps in the treatment train with and without pretreatment. THMFP conditions: pH, not reported; 25°C (77°F); storage time, 6 days.[104]
G = gas contactor
F = dual-media filter
A = GAC adsorber

define further the potential of this combined treatment technique. Preliminary results of these field studies are not promising, indicating that the usefulness of this approach may be limited. The concept of using inert media to support biologic degradation of organic materials in drinking water treatment is also supported by extensive experience with ground treatment, with bank filtration, and slow sand filters in Europe that have each shown effectiveness for removing organic materials during drinking water treatment.[111] A more detailed discussion of the bacteriologic populations in GAC adsorbers and the influence of this unit process on the bacteriologic quality of finished water will be presented in Section IX.

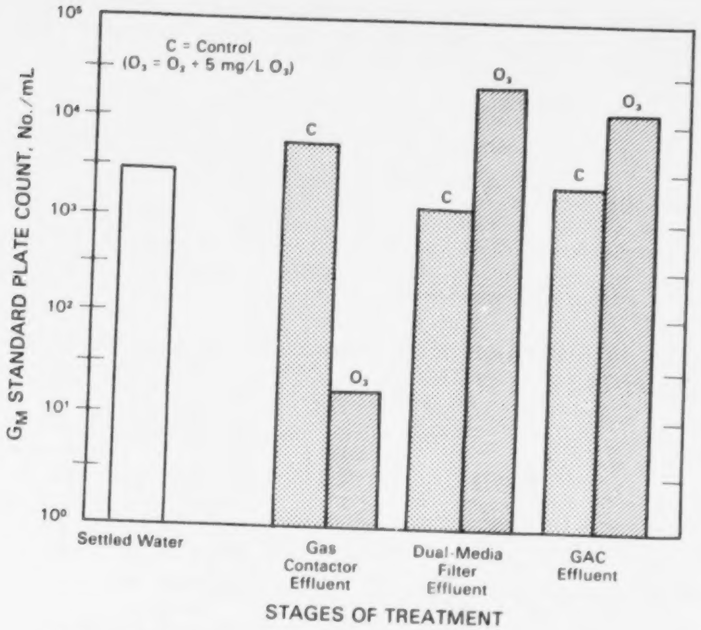

Figure 93. Standard plate counts after various stages of treatment.[104]

Lowering pH

General Considerations—

The pH at which the trihalomethane formation reaction takes place has an influence on the reaction rate, and possibly the yield (see Section III, Subsection Effect of pH). This effect implies, therefore, that if the pH at a given water treatment plant could be lowered (all other conditions being equal), lower THM concentrations would occur at any given time following chlorination. Although this practice would not remove trihalomethane precursor, it would lower the fraction of the potential precursors that could participate significantly in the chlorination reaction, because only those that are reactive at the lower pH would be involved. Two examples of this approach to trihalomethane control are given here.

Experimental Results—

The water treatment plant at Daytona Beach, FL, is a precipitative softening plant with facilities for recarbonation during its treatment process (Figure 64). During the USEPA-sponsored project conducted at this location, tests were made with and without the recarbonation unit process in operation.[85] These results (Table 45) show that during source water chlorination, when the recarbonation basin was in operation and the pH was lowered by 0.9 pH units, the Inst$CHCl_3$ concentration in the finished water was lowered 22 percent compared with the control, and the InstTHM concentration declined 19 percent on a molar basis.

A similar result may have been noted at the Thomas L. Amiss Water Treatment Plant No. 2 in Shreveport, LA.[111] In this case (Table 46), the normal pH range for the control week was 8.4 to 9.4, with a median value of 9.1. During the test week, the pH

TABLE 45. TRIHALOMETHANE FORMATION AT DIFFERENT pH VALUES DURING SOURCE WATER CHLORINATION WITH AND WITHOUT RECARBONATION AT DAYTONA BEACH, FL[85]

Process	Median pH	Source water*		Finished water	
		InstCHCl$_3$, µg/L	InstTTHM, µmol/L	InstCHCl$_3$, µg/L	InstTTHM, µmol/L
Without recarbonation (control)	8.25	NF†	NF	139	1.29
With recarbonation	7.35	NF	NF	109	1.05

*THMFP did not change significantly between these two tests.
†None found.

TABLE 46. COMPARISON OF TRIHALOMETHANE FORMATION AT DIFFERENT pH VALUES DURING CHLORINATION BEFORE RAPID MIX AT SHREVEPORT, LA[111]

Week	Median pH	Rapid mix InstTTHM, µg/L	Median pH	Filtered water InstTTHM, µg/L
Control week	9.1	52	9.1	123
Test week	8.6	87	8.6	115

at the beginning of the treatment was slightly lowered to a range of 8.2 to 8.9 (median 8.6). The resulting data show a slight decline of about 7 percent in the finished water InstTTHM concentrations when the pH was lowered during the test week.

Discussion—

The two studies cited above suggest, on a full-plant scale, that the expected result was obtained from lowering the pH during the reaction between free chlorine and precursor materials. Thus if lower pH values can be maintained and other water quality parameters can be protected at a given water utility (for example, by using some corrosion control technique other than high pH), then a lower fraction of the total potential trihalomethane precursors will react with free chlorine. The result will be lower InstTHM concentrations at any point in the distribution system, as well as lower TermTHM concentrations at the extremities of the distribution system. Considerable caution must be exercised, however, when using this approach for THM control because of the associated potential corrosion problems.

Summary of Trihalomethane Precursor Removal as an Approach to Trihalomethane Control

Advantages of Trihalomethane Precursor Removal—

The generalized reaction between free chlorine and precursor materials is:

FREE CHLORINE + PRECURSORS (HUMIC SUBSTANCES) AND BROMIDE → TRIHALOMETHANES + OTHER BYPRODUCTS

Thus, if the resulting trihalomethane concentrations are controlled by lowering the concentration of precursor materials, free chlorine can still be used as the disinfectant. Such use is advantageous because free chlorine is used at most water treatment plants currently, and water utility managers and operators have confidence in its use and its ability to produce a microbiologically safe water.

Controlling trihalomethane concentrations by treating water to remove precursor materials before disinfection has a second advantage: The general reduction in disinfectant demand caused by the presence of less material with which the disinfectant can react. The data in Figures 94 and 95 show that the effluent from a GAC adsorption column that was removing some trihalomethane precursor material could be disinfected with a lower dose of disinfectant, as demonstrated by a lower number of organisms measured by the standard plate count.

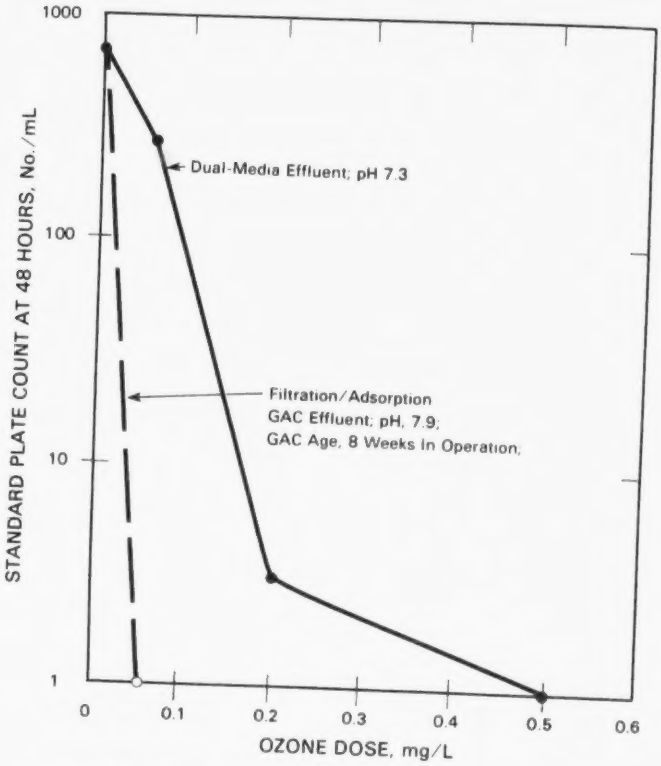

Figure 94. Disinfection with ozone after GAC adsorption to remove trihalomethane precursors. Ozone contact time, 6 min.

A lower disinfectant demand leads directly to a third advantage of this approach to trihalomethane control: The formation of fewer disinfection byproducts of all types. When less disinfectant reacts with less precursor material, not only will the concentration of trihalomethanes decline, but the concentrations of other halogenated byproducts and other nonhalogenated oxidation byproducts will also be lowered. Chlorination of a fresh GAC effluent did not produce significant quantities of other halogenated byproducts (Table 47) as measured by the organic

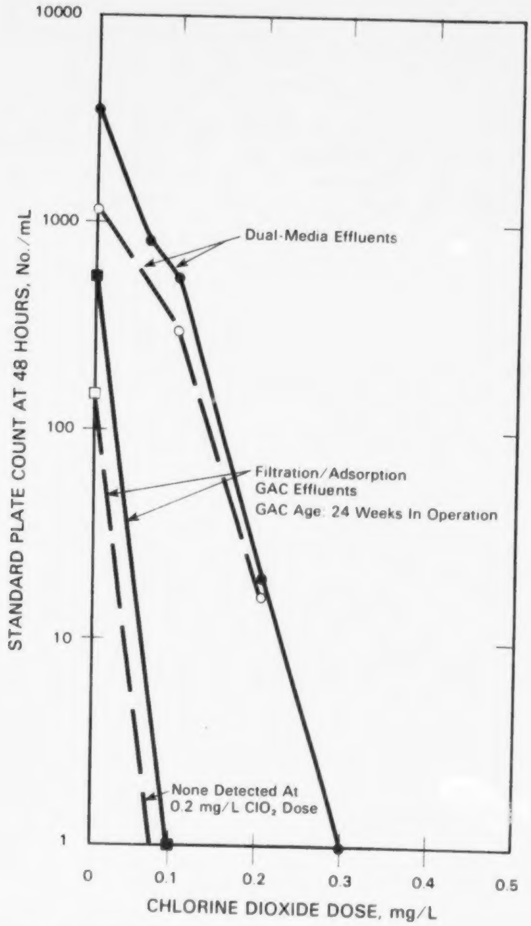

Figure 95. Disinfection with chlorine dioxide after GAC adsorption to remove trihalomethane precursors. pH 7.0–8.1; 22–26°C (72–79°F); ClO_2 contact time, 30 min.

TABLE 47. ORGANIC HALOGEN PRODUCED UPON CHLORINATION OF GAC ADSORBER EFFLUENT AFTER 1 DAY OF OPERATION

Sample	NPOX, μg/L as Cl^-*
Dual-media filter effluent + Cl_2 (control)	**237**
GAC adsorber effluent + Cl_2	**18**

*Blank value is about 10 μg/L OX as Cl^-.

halogen (OX) test.[70] This test shows the general advantage of reducing the concentrations of trihalomethane precursor materials before disinfection. Presumably, the concentrations of other nonhalogenated oxidation byproducts from chlorination would also be lowered if the concentrations of precursor materials were controlled.

Disadvantages of Trihalomethane Precursor Removal—

If disinfection of the source water is required at a given location, practicing trihalomethane precursor removal at some point later in the treatment train will not influence the reaction of the disinfectant with any precursor materials that may be present in the source water. Thus even if the removal of precursor materials is complete, the formation of trihalomethanes will not be completely prevented because of the reaction of chlorine with the trihalomethane precursors in the source water. Because the trihalomethane formation reaction is not usually very rapid, however, the formation of InstTHM probably would not be complete at the point in the treatment train where precursor removal would be practiced; therefore some unreacted precursor would remain and the treatment process would still be somewhat effective. Such a disadvantage in this approach to trihalomethane concentration control is not too serious.

Another disadvantage to precursor removal has been suggested as a result of work performed in the Federal Republic of Germany[114] that has indicated the importance of humic acids in controlling corrosion in water distribution systems. If humic acid is proven to play such a role, then water treatment to control trihalomethanes by humic acid removal might produce a more corrosive water.

SECTION VIII
USE OF ALTERNATIVE DISINFECTANTS

General Considerations

Formation of Trihalomethanes—

Trihalomethanes are formed during drinking water treatment when the free chlorine used as a disinfectant combines with trihalomethane precursors present in the water. One approach to controlling trihalomethane concentrations is the use of a disinfectant other than free chlorine that does not participate in this reaction. Several disinfectants are possible alternatives to free chlorine: chloramines (combined chlorine), chlorine dioxide, ozone, potassium permanganate, hydrogen peroxide, bromine chloride, bromine, iodine, ferrate ion, high pH, and ultra-violet radiation. Of these, chloramines, chlorine dioxide, and ozone are the most commonly used in drinking water treatment practice today and have been studied in detail.[115] Because of the interest in using bromine chloride for the disinfection of wastewater, a brief USEPA in-house evaluation of that disinfectant was made. One literature reference to the use of iodine is also included.

Biocidal Activity—

The primary reason for the use of disinfectants in the treatment of drinking water is to ensure the destruction of pathogenic microorganisms during the treatment process, thereby preventing the transmission of disease by drinking water. Secondarily, the presence of a disinfectant in the water distribution system helps to maintain the quality of water by preventing the growth of nuisance microorganisms. An extensive examination of the impact of various treatment modifications on the bacteriologic quality of finished drinking water is provided in Section IX.

Disinfection Kinetics and Comparative Efficiencies—Biocidal activity by chemical disinfectants has frequently been considered a kinetic process similar to a chemical reaction, the microorganism being considered as one of the substances involved in the reaction. The effectiveness or efficiency of biocidal agents is determined by the rate at which the reaction or killing of the microorganism population proceeds. The comparative biocidal efficiencies of disinfectants are frequently expressed as the relative concentration (mg/L) of different disinfectants needed to obtain equivalent disinfection rates, or as the relative inactivation rates produced by the same concentration of different disinfecting agents. Most of this information has been obtained by laboratory experimentation under carefully controlled conditions, which include clean systems, the absence of extraneous disinfectant-demanding substances, and the use of pure cultures of the microorganism under study. The presence (in solution) of materials exerting disinfectant demand is likely to change disinfection efficiencies by way of competing reactivation mechanisms. This effect complicates extrapolations from experiments with clean systems to expected water utility performance. Nevertheless, comparisons of disinfectant performance under laboratory conditions are instructive.

A typical curve from such an experiment is shown in Figure 96. Data from the results of a number of such experiments conducted using different disinfectants at various concentrations can be used to construct plots of the type shown in Figure 97. As indicated, these results show the exposure times and concentrations of several

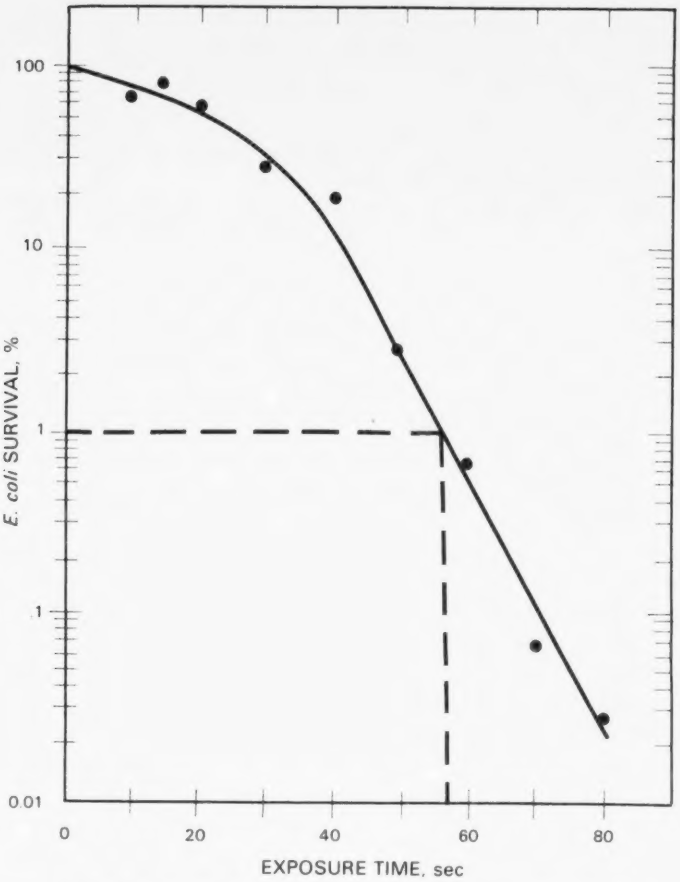

Figure 96. Destruction of *E. coli* at pH 7.0, 15°C (59°F), in the presence of 0.16 mg/L chlorine dioxide. This example shows the method used to determine points plotted in Figures 97 and 98.[116]

disinfectants needed to produce a given level of inactivation of a given microorganism. Figure 97 is a composite of results obtained in one laboratory over a period of years using consistent experimental methods and microorganisms.[116,117] The results show that chlorine dioxide at pH 7 and HOCl at pH 6 produce similar rates of inactivation of *Escherichia coli*. Hypochlorite ion (OCl^-) at pH 10 was less effective, and monochloramine at pH 9 and dichloramine at pH 4.5 were even less so. From the data shown in Figure 97, the degree of difference in efficiency between the disinfectants could be calculated and expressed quantitatively. For example, HOCl at pH 6 is 35 times as effective as OCl^- at pH 10. A similar plot showing virucidal efficiency of these disinfectants for poliovirus 1 is shown in Figure 98. Note that higher disinfectant concentrations and longer contact times in general are needed for inactivation of poliovirus 1 than for *E. coli*. The differences are on the order of less than 1 to 2 orders of magnitude, depending on the disinfectant used. Also, the difference in efficiency between HOCl at pH 6 and OCl⁻ at pH 10 is only about 4-fold, and the efficiency order of the two types of combined chlorine is reversed.

Studies from which similar curves can be prepared have not been done using ozone as the disinfectant. The main reason is that ozone is such a powerful and unstable disinfectant that limitations on sampling times and ozone measurements make obtaining good experimental results difficult. In spite of this difficulty, ozone does inactivate microorganisms at a high rate.

For instance, Walsh et al.[118] reported *E. coli* inactivation rates after 10 seconds' response to ozone ranging from 99.999% at 0.239 mg/L to 86% at 0.014 mg/L. Inactivation of poliovirus 1 after 10 seconds' response to ozone ranged from >99.993% at 0.28 mg/L to >99.4% at 0.012 mg/L.

Factors Affecting Comparative Disinfection Efficiencies—Microorganism Effects—As shown in Figures 97 and 98, neither the order of efficiency nor the degree of difference between the disinfectants is the same for *E. coli* as for poliovirus 1. Further evidence of such differences is shown in Table 48. This study examined the inactivation rates of six different enteroviruses by HOCl at pH 6 and by OCl⁻ at pH 10.[119] The results indicate that the degree of difference in disinfection efficiency of HOCl at pH 6 and of OCl⁻ at pH 10 ranged from 5-fold for Coxsackie A9 virus to 192-fold for ECHO 1 virus. Also note the occurrence of differences of 10-fold and 53-fold in the rates of inactivation of other viruses by HOCl at pH 6 and OCl⁻ at pH 10.

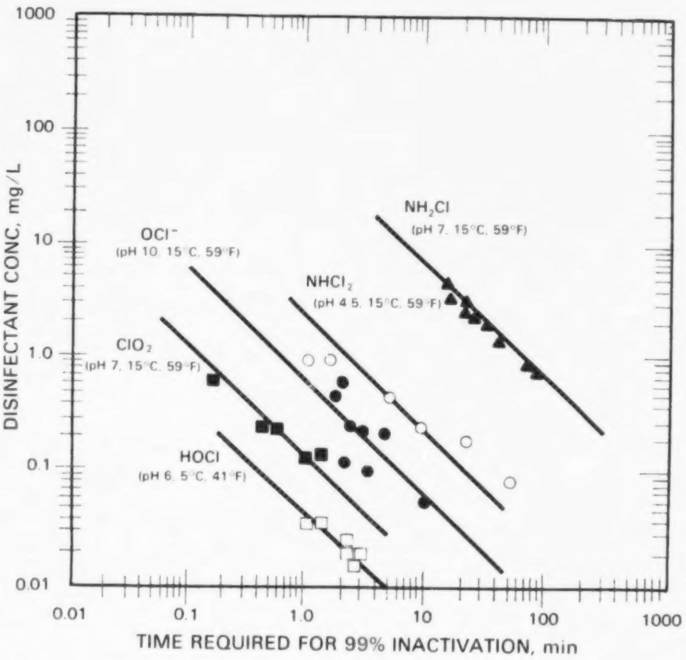

Figure 97. Inactivation of *E. coli* (ATCC 11229) by free and combined chlorine species and chlorine dioxide.[116,117]

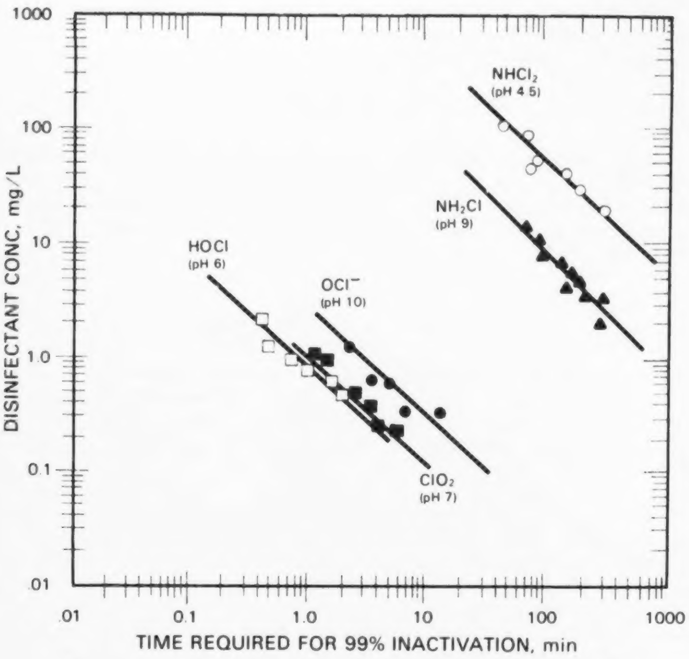

Figure 98. Inactivation of poliovirus 1 (Mahoney) by free and combined chlorine species and chlorine dioxide at 15°C (59°F).[116,117]

TABLE 48. VIRUS INACTIVATION BY FREE RESIDUAL CHLORINE[119]

	Min. required for 99% inactivation at 5.0 ± 0.2°C (41 ± 0.4°F)		
Virus strain	**pH 6.0**	**pH 10.0**	**Ratio***
Coxsackie A9 (Griggs)	0.3	1.5	5
ECHO 1 (Farouk)	0.5	96.0	192
Polio 2 (Lansing)	1.2	64.0	53
ECHO 5 (Noyce)	1.3	27.0	21
Polio 1 (Mahoney)	2.1	21.0	10
Coxsackie B5 (Faulkner)	3.4	66.0	19

*Time required at pH 10.0/time required at pH 6.0.

Disinfectant Chemistry Effects—Assessing the efficiencies of different free and combined chlorine species also is complicated by the nature of the chemical reactions that determine the chemical species present and the chemical equilibriums established under various pH conditions. For instance, in the reaction

$$\mathrm{HOCl} \rightleftharpoons \mathrm{H^+} + \mathrm{OCl^-} \qquad \text{[Eq. 10]}$$

a rapidly achieved equilibrium exists that is drastically influenced by pH. At pH 10, however, approximately 0.5 percent of the free residual chlorine is still present as

HOCl, and because it is a much more powerful biocide than OCl^-, its presence could substantially influence the biocidal activity observed.

Similarly, Equation 11 is reversible,

$$HOCl + NH_3 \rightleftharpoons NH_2Cl + H_2O \qquad [Eq.\ 11]$$

and a solution of 2 mg/L NH_2Cl is estimated to be 0.58 percent hydrolyzed (0.58 percent HOCl) at pH 7 and 25°C (77°F).[120] Because of the much higher biocidal efficiency of HOCl, its influence on the disinfection rate observed could be substantial and could explain the influence of pH on the biocidal efficiency of monochloramine.

Furthermore, the equation:

$$H^+ + 2NH_2Cl \rightleftharpoons NH_4^+ + NHCl_2 \qquad [Eq.\ 12]$$

indicates that although mostly monochloramine is formed when excess ammonia is present at high pH (>8), addition of hydrogen ion (lowering pH) will cause formation of dichloramine, with the position of this equilibrium being determined by the pH of the treated water. Thus with chlorine and chloramines, pure species are never present, and pH determines their identities. The influence of pH therefore cannot be experimentally separated from species effectiveness for disinfection.

Nevertheless, in the case of chlorine, disinfection efficiency declines rapidly as the pH is increased from 7 to 9. The efficiency of chlorine dioxide also changes substantially over this pH range; but in contrast to chlorine, the effectiveness increases as the pH increases (Figure 99).[116] In this case, the change appears to be in microorganism sensitivity rather than in disinfectant species present, because unlike chlorine, chlorine dioxide does not dissociate or disproportionate into different chemical species within this pH range. In earlier studies, a similar effect was shown with *E. coli* (i.e., more rapid inactivation at pH 8.5 than at lower pH by equivalent concentrations of chlorine dioxide).[121]

The pH of the water also affects ozone chemistry. At high pH values, ozone decay is accelerated, proceeding through hydroxyl radical intermediates; thus, the pH of the water being treated may also influence ozone effectiveness.

Dissolved Salt Effects—In 1972, Scarpino et al. reported that OCl^- was a more efficient virucide than HOCl against poliovirus 1.[122] Results of subsequent unpublished studies indicated that 0.05M KCl, present in the buffer used in the OCl^- experiments, was responsible for the increased virucidal efficiency of OCl^-. Engelbrecht et al., in further studies in this area, confirmed and extended the earlier studies and showed that 0.05M KCl enhanced the virucidal efficiency of both OCl^- and HOCl.[119] Sharp and co-workers have also confirmed this effect and shown that similar results are produced by the presence of NaCl and CaCl.[123-125] This effect was not seen in *E. coli* disinfection studies reported by Scarpino et al., although the same KCl-containing buffer was used in these studies.[122]

From the information provided above, ranking these disinfectants precisely and quantitatively as to their biocidal efficiency is not possible. A major reason for this is that various microorganisms react differently, and the same microorganism may react differently under various experimental conditions. Note that the effects described above influence the *rate* at which microorganism inactivation occurs, not whether or not inactivation occurs at all.

Adequacy of Chlorine-Ammonia Treatment—Despite the generally weaker biocidal efficiency of chloramines, the chlorine-ammonia treatment process has been used successfully for primary disinfection for years by a number of utilities. The chloramine formation, as accomplished in these treatment plants, differs significantly from the procedures used in preparing chloramine for use in the

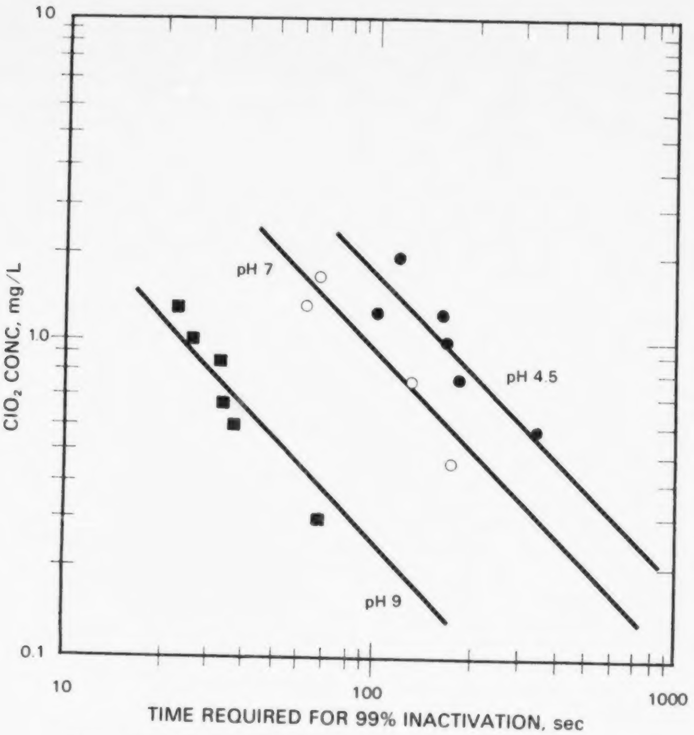

Figure 99. Effect of pH on inactivation of poliovirus 1 (Mahoney) by chlorine dioxide at 21°C (70°F).[116]

laboratory chloramine disinfection studies described above. In the experimental work, the chloramines were preformed and the microorganisms were added subsequently. In chlorine-ammonia treatment for primary disinfection, as practiced in the field, ammonia and chlorine are added to the water either simultaneously or in close succession. The rate of conversion of free chlorine to chloramines depends on pH, temperature, and the chlorine/ammonia ratio present.

Although the reaction to form chloramines occurs in hundredths of a second at high temperatures and optimum pH (8.3), it can occur at much slower rates at lower temperatures and lower or higher pH values. Thus free chlorine could be present for several minutes and result in rapid inactivation of microorganisms (particularly at lower pH values) because of the presence of free residual chlorine in the form of HOCl. This possibility was suggested by Hoather and Houghton as an explanation for the much faster bactericidal action observed in ammonia-chlorine treatment than could be shown using preformed chloramines.[126,127] In more recent pilot-scale chloramination studies involving both clean water and tertiary effluent, Selleck et al. ascribed the initial rapid phase of bactericidal action during chloramine treatment to oxidation reduction reactions occurring between the chlorine and substances present in the water, rather than to unreacted free chlorine.[128] They postulated that highly reactive, short-lived, free radicals produced during the oxidation of ammonia nitrogen may be responsible for the rapid inactivation of bacteria.

From these studies, the much slower experimental inactivation rates shown by preformed chloramines may not be directly relevant to chloramine treatment in the field. The enteroviruses are, however, much more resistant than coliforms to both free residual chlorine and chloramines (see Figures 97 and 98). If, in a particular field situation, the margin of safety provided by free residual chlorination is minimal, conversion to chloramine treatment might further reduce the disinfection efficiency. Therefore, whether or not the initial rapid inactivation phase would be of sufficient duration to ensure virus destruction would depend on the source water and other treatment processes used. Because of this uncertainty, conversion from free chlorine to chloramine treatment for primary disinfection should be considered with caution. For this same reason, the Trihalomethane Regulation[3] placed the use of chloramines at the discretion of the Primacy Agency, to be considered on a case-by-case basis.

Application of Laboratory Study Results to Field Situations—Although information derived from laboratory studies is useful in assessing the biocidal efficiency of disinfectants, other factors are important in the application of this information to actual drinking water treatment in the field. In water treatment, pure cultures of organisms are not present as clean suspensions in a medium free of extraneous materials that might react with the disinfectant used, thereby destroying or altering its biocidal capability. Rather, in the field, a variety of microorganisms are present in their natural state, suspended in a medium containing a variety of other solid and dissolved materials, some of which can have pronounced effects on disinfectant concentration and activity. Because of these effects, disinfection in the field does not operate as a constant rate process as it does in laboratory studies, changing the shape of the decay curves and perhaps even the order of disinfectant effectiveness observed. A particularly good example of changing the order of effectiveness might be the influence of disinfectant demand rapidly depleting a free chlorine residual while combined chlorine remains at a higher level for a longer period of time providing better overall effectiveness. Nonetheless, some of these conditions can be simulated in laboratory experiments and can provide information that will be more relevant to actual practice.

For example, protection of microorganisms has been considered because their association with particulate matter could result in their being shielded from disinfectant action. This possibility has been the major consideration in establishing a turbidity limit for drinking water. Hoff has recently provided direct evidence of such protective effects.[129] Poliovirus association with washed-cell debris has been shown to offer substantial protection against inactivation by HOCl when compared with freely suspended virus (Figure 100). Similarly, the data in Figure 101 show that coliforms associated with washed primary effluent solids are inactivated by HOCl much more slowly than clean suspensions of laboratory-grown *E. coli*. Hijkal et al. have also shown that poliovirus associated with fecal material is provided substantial protection against inactivation by free chlorine.[130]

Furthermore, Foster et al. showed that cell-debris-associated virus also was protected from inactivation by ozone, the most efficient biocide under consideration.[131] Ozone levels in excess of 2 mg/L failed to completely inactivate viruses associated with cell debris in 30 seconds. In longer term experiments, viruses could be detected even after exposure for 75 minutes to an initial ozone level of 2.5 mg/L. Comparable information for chlorine dioxide and chloramines is not yet available, but in view of the ozone results, they will likely show the same limitations in efficiency for inactivating microorganisms associated with such solids.

Summary—

Because of the influence of environmental factors on disinfection, precise rankings of the three alternative disinfectants—ozone, chlorine dioxide, and chloramines—cannot be made. In general, however, ozone and chlorine dioxide are

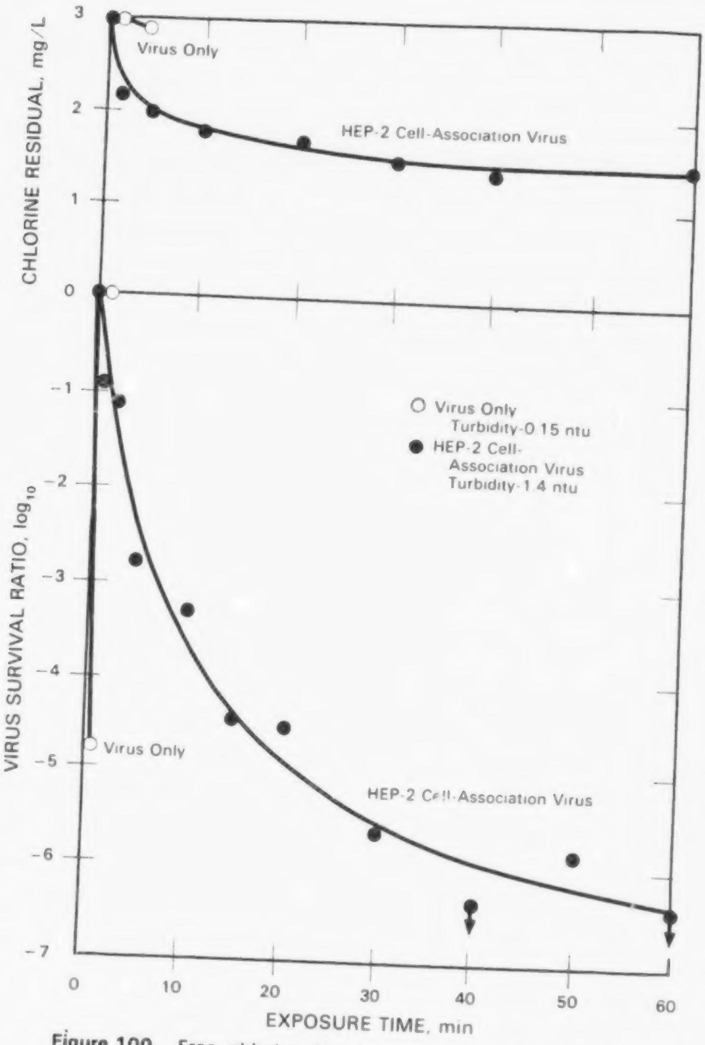

Figure 100. Free chlorine inactivation of freely suspended poliovirus and poliovirus associated with cell debris. pH 6.0; 5°C (41°F).[129]

ranked as strong disinfectants that are nearly equal to or better than free chlorine, even at low pH. Furthermore, in contrast to free chlorine, the disinfecting power of neither is reduced by increasing pH; in fact, with chlorine dioxide, the opposite is true. Chloramines are generally ranked as disinfectants that are weaker than free chlorine at all pH values. But they are adequate in many cases, and some utilities have been successfully using chloramines for some time. Furthermore, the equilibrium between monochloramine and dichloramine, which have different disinfecting powers, is influenced by pH.

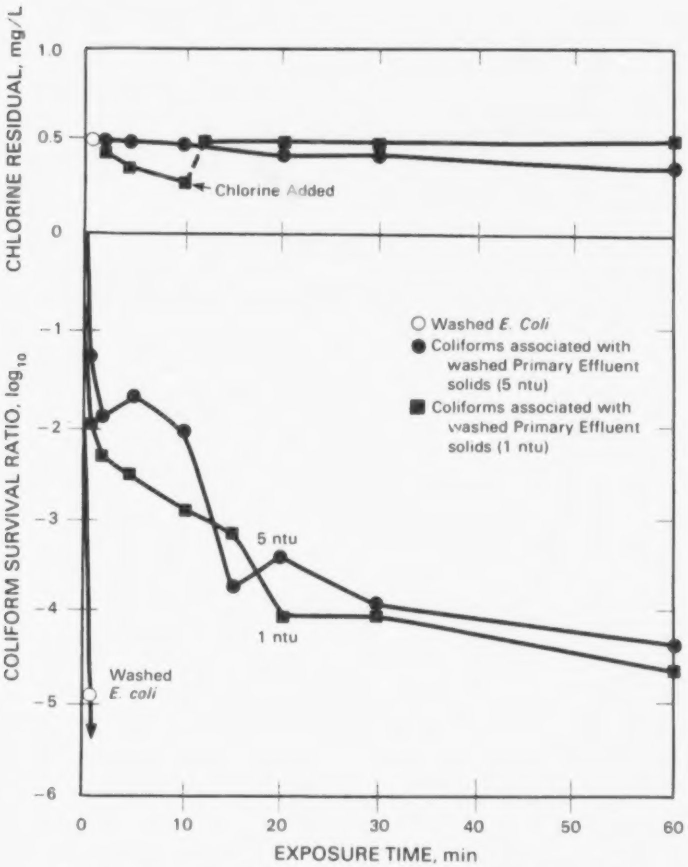

Figure 101. Free chlorine inactivation of washed, laboratory-grown *E. coli* and coliforms associated with primary effluent solids. pH 6.0;5°C (41°F).[129]

Experimental Results

Formation of Trihalomethanes*—

Chloramines (Combined Chlorine)—An in-house USEPA study compared the formation of chloroform in Ohio River water when free chlorine and combined chlorine were the disinfectants. In this study, ammonia-nitrogen was added to the Ohio River water before the introduction of chlorine in an attempt to prevent as much free chlorine as possible from being present in the sample. The results of this study were presented in Figure 14 (Section III). These data show little development of chloroform during the 70 hours of exposure when combined chlorine was the disinfectant. In contrast, much higher concentrations of chloroform were formed in the presence of a free chlorine residual. At many water treatment plants where chloramines were used alone or where ammonia was added after a period of free chlorination to form chloramines, data have also shown lower resulting trihalomethane concentrations when compared with situations in which free chlorine was the disinfectant. Several of these studies are summarized in this subsection.

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*In many of these studies, the influence of the disinfectant on both the formation of trihalomethanes and the inactivation of microorganisms was studied. As noted previously, the influence of various treatment modifications on bacteriologic quality will be presented in Section IX.

Figure 102 shows a block diagram of one of the water treatment plants of the St. Louis County Water Department.[132] In this case, 8 hours of free chlorine residual existed before the addition of ammonia and more chlorine to carry a combined residual throughout the distribution system. Little if any increase in chloroform concentration occurred during the 12-hour transit time from the treatment plant to a storage tank (Table 49).

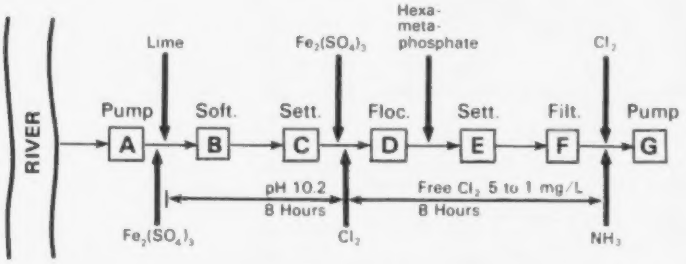

Figure 102. Block diagram of a St. Louis County water treatment plant.[132] (Adapted from AWWA Water Quality Technology conference—IV PROCEEDINGS [December 5-6 1976] by permission. Copyright 1976, the American Water Works Association.)

TABLE 49. INFLUENCE OF AMMONIA ADDITION ON TRIHALOMETHANE FORMATION AT THE ST. LOUIS COUNTY WATER COMPANY[132]

	Finished plant water		Storage tank 12 hours away			
Date	$CHCl_3$ µg/L	$CHBrCl_2$ µg/L	Combined Cl_2 res. mg/L	NH_3-N mg/L	$CHCl_3$ µg/L	$CHBrCl_2$ µg/L
9/20/76	38	12	1.8	0.55	34	8
9/22/76	36	11	1.6	0.50	35	12
9/23/76	34	12	2.2	0.35	36	13
9/27/76	38	12	2.3	0.40	35	12

One of the water utilities included in a project managed by the Ohio River Valley Water Sanitation Commission (ORSANCO) was Beaver Falls, PA.[18] At this water utility, breakpoint chlorination was temporarily halted sometime between February 15 and 22, 1978. As a result of this alteration in treatment practice, a considerable decline in the InstTTHM concentration occurred (Table 50), even though a rise in water temperature in the spring months would usually cause a rise in trihalomethane concentrations. When breakpoint chlorination was reinstated in June, the InstTTHM concentration rose significantly.

TABLE 50. INFLUENCE OF ENDING BREAKPOINT CHLORINATION TEMPORARILY AT BEAVER FALLS, PA[18]

	Clearwell		
Date, 1978	**Measured free Cl_2 residual, mg/L**	**Total Cl_2 residual, mg/L**	**InstTTHM, µg/L**
1/3	0.8	0.9	52
1/13	0.9	1.0	48
1/18	1.0	1.2	61
1/25	0.8	0.9	45
2/8	0.8	0.9	52
2/15	0.5	0.5	41
2/22	0.4*	1.2	7†
3/1	0.5*	1.2	7
3/15	<0.1*	1.2	11
3/29	NR‡	0.9	12
4/12	0.1*	1.1	12
4/26	NR	1.2	10
6/27	1.6	NR	126§

*Some permanganate present, measured as free Cl_2

†Breakpoint chlorination stopped.

‡Not run.

§Breakpoint chlorination resumed.

During the ORSANCO project, InstTTHM concentrations were determined monthly at several participating water utilities treating various qualities of river water.[18] Of these, five maintained a relatively high free chlorine residual in the finished water, and two practiced marginal chlorination. Although the source waters were different, the InstTTHM concentration was significantly lower for any given month in the two water utilities that maintained relatively high chloramine residuals (Wilkinsburg-Penn Joint Water Authority and Fox Chapel Authority) than in the five utilities that maintained relatively high free chlorine residuals (Figure 103).

During this same project, investigations were carried out at the Hays Mine Plant of the Western Pennsylvania Water Company.[18] At this plant, routine treatment included chlorination of both source water and filtered water. Because of the varying concentration of ammonia in the source water, a free chlorine residual was present sometimes, and a combined chlorine residual occurred at other times. Although no true control existed in this study, an average of only 22 µg/L InstTTHM was present in the finished water when the ammonia was present in the source water, contrasted to 42 µg/L InstTTHM when a free chlorine residual existed (Figure 104). This difference was probably caused by the presence of the combined chlorine residual.

The Louisville Water Company has tried several alternative treatment techniques involving various disinfectants and combinations of disinfectants in an attempt to control the trihalomethane concentrations in their distributed water.[133-135] Their treatment scheme consists of plain sedimentation with no coagulant, followed by coagulation and sedimentation, softening, and dual-media filtration. The first modification, in August 1977, involved chlorination of the coagulation basin influent and the addition of chlorine and ammonia in the clearwell following filtration. Under these conditions, the InstTTHM concentration in the clearwell was about 150 μg/L, but no further increase in trihalomethane concentrations occurred in the distribution system because of the absence of a free chlorine residual.

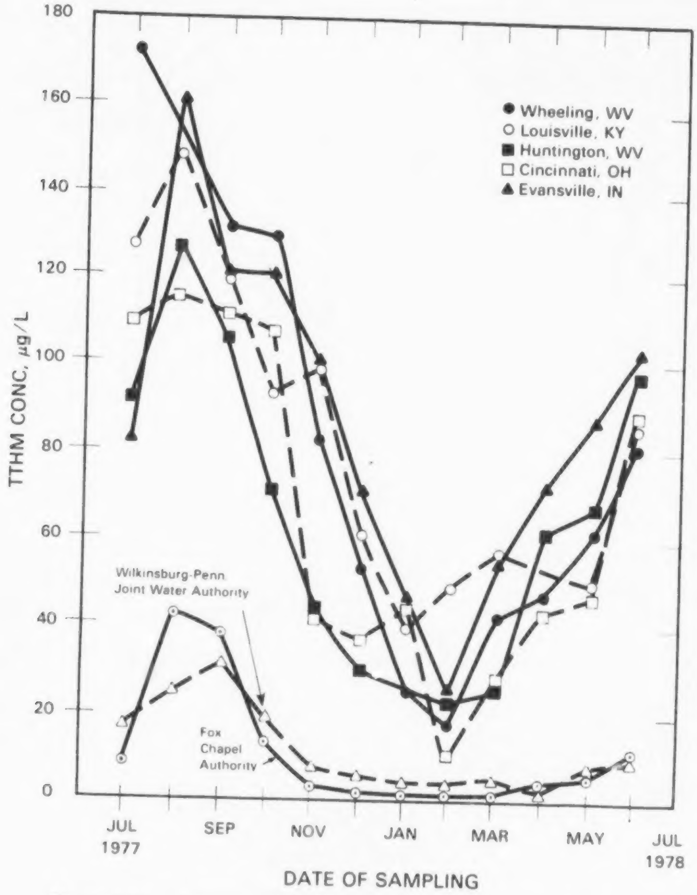

Figure 103. Seasonal variation in finished water TTHM concentrations for treated surface waters.[18]

The second test, conducted in October 1977, involved the movement of the point of ammonia addition from the clearwell to the softening basin. This step reduced the InstTTHM concentration in the clearwell to about 95 μg/L, with only about an 8 percent increase in trihalomethane concentrations from the effluent of the softening basin through the distribution system.[133]

Currently, the following treatment is practiced: Potassium permanganate and copper sulfate are added to the plain settling basin, as needed, to control taste, odors, and algae; chlorine is added to the effluent of the coagulation-sedimentation basin, and ammonia is added 10 minutes later. This practice has reduced the InstTTHM concentration in the distribution system to approximately 15 μg/L.[134,135] Although no controls were available during these tests, the changes in trihalomethane concentrations were most probably caused by the treatment changes. A possible future summertime operation involves combining chlorine dioxide with ammonia. This procedure is discussed later in this section under Chlorine Dioxide.

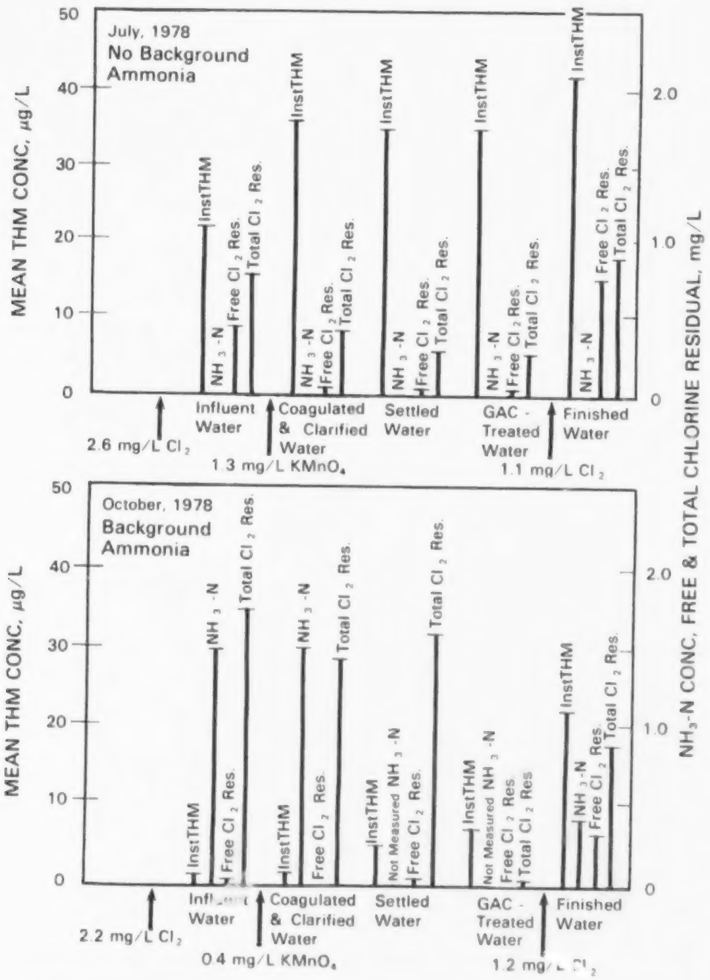

Figure 104. Influence of ammonia nitrogen in the source water on trihalomethane concentrations at the Western Pennsylvania Water Company, Pittsburgh, PA.[18]

The Jefferson Parish Water Department has used combined chlorine as the primary disinfectant for some time. Brodtmann et al. reported on the InstTTHM concentrations in the Jefferson Parish distribution system as compared with the THMFP concentration measured with free chlorine in the samples in the sand filter effluent.[136] During an 18-month period (January 1978 to June 1979), some 19 samples per month were analyzed and averaged. The data in Table 51 show how much lower the monthly mean InstTTHM concentrations were in the distribution system with combined chlorine present than they would have been with the temperature, pH, and storage time shown for the free-chlorine-treated sample, as indicated by the THMFP concentration.

TABLE 51. COMPARISON OF TTHM's IN AMMONIATED DISTRIBUTION WATER WITH THMFP OF CHLORINATED SAND FILTER EFFLUENT AT JEFFERSON PARISH, LA[136]

Month	Number of distribution samples analyzed	Mean distribution water InstTTHM, μg/L	Sand filter effluent THMFP,* μg/L
1978:			
January	15	3.2	241
February	20	3.1	271
March	20	5.0	269
April	15	2.8	302
May	20	5.2	†
June	25	4.2	†
July	15	23.9‡	319
August	25	7.3	232
September	20	8.8	191
October	20	7.3	250
November	10	7.2	211
December	20	6.1	173
1979:			
January	25	4.2	171
February	10	3.0	†
March	20	1.9	†
April	20	3.4	203
May	25	6.2	365
June	20	7.9	272

*Five days, 30°C (86°F), pH 10; initial free Cl_2, 10 mg/L.
†No data collected during this period.
‡Ammoniator out of service; free chlorine residual present in part of distribution system.

Water treatment at Huron, South Dakota, consisted of adding to James River Water alum and polyelectrolytes for coagulation and lime for softening, followed by settling, recarbonation, filtration and disinfection with chloramines.[137] Before 1979, when breakpoint chlorination was practiced, the TTHM concentrations in the distribution system sometimes exceeded 300 μg/L. Following a USEPA sponsored project, ammonium sulfate is now being added to produce combined chlorine. Trihalomethane reductions ranging from 72 to 79 percent occurred at two places in the distribution system immediately following institution of the new treatment.

At the University of Texas at San Antonio, research is under way to investigate methods of reducing the trihalomethane formation while maintaining effective disinfection by achieving instantaneous and total mixing of the disinfectant following dosing, preventing trihalomethane formation by reducing reaction time.[138] Disinfectant is introduced by means of a high-energy (G = about 40,000 sec^{-1}), in-line mixer to a 410-m^3/day (75-gpm) flow stream. After 16 seconds of contact time, the water passes through a second high-energy, in-line mixer. Flow continues in a pipe loop system for 55 seconds to provide short, but precisely known contact times.

Longer contact times for disinfection or trihalomethane formation are obtained by collecting samples of water discharged from the pipe loop and holding them for the desired time period.

This project studied the formation of trihalomethanes in disinfection systems involving chlorine only, chlorine followed by addition of ammonia 16 seconds later, ammonia followed by addition of chlorine 16 seconds later, or chlorine dioxide. Addition of ammonia after 16 seconds eliminated the free chlorine residual, thereby reducing the trihalomethane formation (Table 52). These data show that reducing trihalomethane formation by limiting the free chlorine contact time in this type of mixing system is feasible.

TABLE 52. TRIHALOMETHANE FORMATION IN LAKE WATER PASSED THROUGH A HIGH-INTENSITY MIXING SYSTEM[138]

Disinfectant dose, mg/L	System	pH	TermTTHM,* μg/L	Free chlorine residual at 48 hr, mg/L
0	No disinfection (control)		<0.1	0
0.5	Chlorine	—	6.3	0.1
0.5	Chlorine + ammonia†	7.65	2.5	0
0.5	Ammonia + chlorine†	—	0.13	0
0.5	Chlorine dioxide	—	2.7	—
1.5	Chlorine	7.7	119	0.3
1.5	Chlorine + ammonia†	7.6	7.4	0
1.5	Ammonia + chlorine†	—	0.43	0
5.0	Chlorine	7.5	179	2.5
5.0	Chlorine + ammonia†	7.85	10.2	0
5.0	Ammonia + chlorine†	—	4.3	0

*48 hours, 14°C (57°F) to 17°C (63°F).
†Ammonia dose equal to chlorine dose in mg/L.

The North Jersey District Water Supply Commission compared free and combined chlorine for trihalomethane formation control during 1979 (unpublished data). Flow from the Wanaque Reservoir was divided between two 1.9-m (74-in) diameter, cement-lined steel mains, one of which was treated with free chlorine, and the other with chlorine plus ammonia. The flows were divided for 6 hours and then combined downstream. With ammonia following free chlorine injection, the total trihalomethane concentration at the juncture reached 6 μg/L; without ammonia, the total trihalomethane concentration was 38 μg/L at this same point.

Lange and Kawczynski, in their efforts to control TTHM concentrations at the Contra Costa County Water District, experimented with the use of chloramines.[20] They conducted jar tests arranged to resemble treatment at the water plant with source water chlorination, ammonia being added to the chlorinated water at a weight ratio of 3/1 (NH_3/Cl_2). The data (Table 53) show that the addition of ammonia did arrest the formation of trihalomethanes. But because the high bromide concentration caused a rapid formation of bromine-containing trihalomethanes, very little time could be allowed to elapse between the addition of chlorine and ammonia if significant reductions in InstTTHM concentrations were to be achieved. The

California State Department of Health required that under these circumstances, a free chlorine residual be maintained for a minimum of 10 minutes before the addition of ammonia. Other Primacy States may have similar requirements.

TABLE 53. RESULTS OF CHLORAMINE STUDIES AT CONTRA COSTA, CA, SEPTEMBER 1977[20]

Cl_2 contact time before adding NH_3, hr	pH	Trihalomethanes, $\mu g/L$				TTHM, $\mu g/L$
		$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	
0	7.0	3	2	1	<1	6
0.5	7.0	15	16	39	50	120
1.0	7.0	7	18	45	55	125
1.5	7.0	8	20	51	60	139
4.0	7.0	9	26	58	50	143
Control treatment sample (excess Cl_2)	8.2	5	18	84	189	296

Siemak et al. reported on the efforts of several California utilities to control trihalomethane concentrations.[139] They briefly mentioned a study by the Casitas Municipal Water District on use of the addition of ammonia. In a summary of this work, they reported that the InstTTHM concentration was reduced from about 150 $\mu g/L$ when chlorination only was used, to approximately 75 $\mu g/L$ when post-ammoniation was practiced to produce a chloramine residual.

Sontheimer, reporting on the work of Sander and Oehler at the Stuttgart Water Works, Federal Republic of Germany, presented data showing that when breakpoint chlorination was no longer practiced at this utility, the resulting trihalomethane concentrations were significantly lowered (Table 54).[140] When breakpoint chlorination was not used, chlorine was added in small amounts in a stepwise fashion throughout the treatment train without ever producing a free chlorine residual.

TABLE 54. EFFECT OF HALTING BREAKPOINT CHLORINATION AT STUTTGART, FEDERAL REPUBLIC OF GERMANY[140]

	Breakpoint chlorination		Nonbreakpoint chlorination	
	River water	Sedimentation basin effluent	River water	Sedimentation basin effluent
NH_4^+, mg/L	1.2	0.03	0.9	0.4
TTHM, $\mu g/L$	0.2	53	0.1	5

These 12 studies all confirm that trihalomethane formation will be reduced if chloramines rather than free chlorine are used for disinfection.

Chlorine Dioxide—To investigate the reaction of chlorine dioxide with typical trihalomethane precursors, an in-house USEPA study was conducted using humic acid* treated with chlorine dioxide that was prepared as described in Section VI, Subsection Oxidation.[39] Generated in this manner, the chlorine dioxide solution was nearly devoid of free chlorine.

In these experiments, humic acid solution (5 mg/L) was dosed with 8 mg/L chlorine dioxide. After 48 hours of contact time, 1.7 $\mu g/L$ of chloroform was formed

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*See Section VII, Subsection Oxidation (Chlorine Dioxide) for a description of humic acid preparation.

(Figure 105), but no other trihalomethane species occurred. For comparison, a similar humic acid solution was dosed with 8 mg/L of free chlorine. In the same time period, 108 μg/L of chloroform (Figure 105) and 1.5 μg/L of bromodichloromethane were formed—about 110 μg/L TTHM. This study indicates conclusively that chlorine dioxide does not produce trihalomethanes from precursor materials that will react with free chlorine to produce trihalomethanes.

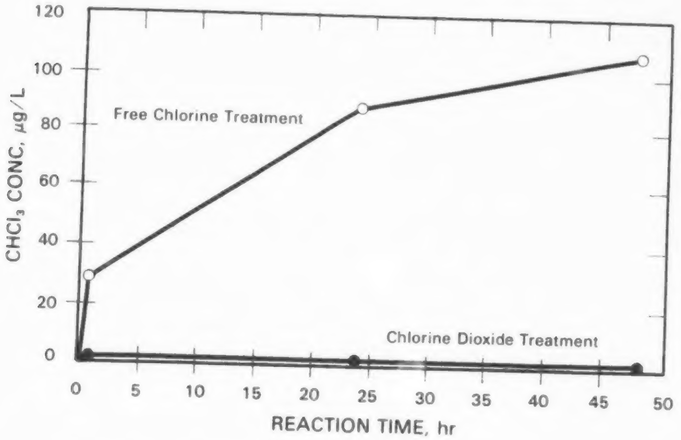

Figure 105. Chloroform formation in water containing 5 mg/L humic acid dosed with chlorine-free chlorine dioxide or free chlorine.[39]

In another experiment (Table 55) chlorine-free chlorine dioxide was added to Ohio River water.[16] Again, low concentrations of trihalomethanes were formed. In this experiment, the companion control dosed with free chlorine was not run, but many previous experiences have shown that Ohio River water will produce significant concentrations of trihalomethanes upon chlorination. These results again indicate that in a natural medium, chlorine-free chlorine dioxide does not produce significant concentrations of trihalomethanes.

During normal continuous flow operation, chlorine dioxide is usually generated by adding chlorine to sodium chlorite in a concentrated stream. Because this reaction proceeds best at a low pH, hydrochloric acid or excess chlorine is added to reduce the solution pH. In either case, the chlorine dioxide produced contains some chlorine (more if excess chlorine is used).

At the USEPA Evansville, IN, project, stoichiometric quantities of NaOCl, $NaClO_2$, and HCl were mixed together in a chlorine dioxide generator in an attempt to produce chlorine dioxide with little chlorine in it.[63] On the average, the generator effluent produced chlorine dioxide containing 9.5 percent chlorine and 56 percent chlorite (of the total oxidants) by weight.

Although the presence of chlorine in this mixture suggests that trihalomethanes would be formed under these circumstances, as previously discussed in Section VII, Subsection Oxidation (Experimental Results), chlorine dioxide alters certain trihalomethane precursors so that the yield of trihalomethanes is reduced when free chlorine reacts with them. Thirteen tests were performed with various doses of chlorine dioxide and free chlorine to determine how these mixtures would behave when treating Ohio River water that had been coagulated, settled, and passed through a dual-media filter in the USEPA pilot plant. Although more research is needed to elucidate the reason, the resulting trihalomethane concentrations are generally inversely related to the chlorine dioxide/free chlorine ratio (Table 56). Significant concentrations of trihalomethanes would not be expected under these circumstances, because a well operated chlorine dioxide generator using acid for pH control can produce chlorine dioxide containing relatively small quantities of free chlorine.

TABLE 55. TRIHALOMETHANE PRODUCTION WITH CHLORINE-FREE CHLORINE DIOXIDE ADDED TO OHIO RIVER WATER[39]

ClO_2 dose, mg/L	ClO_2 residual, mg/L	Contact time, hr	Chloroform, µg/L
0	0	—	<0.2
1.4	0.7	0.5	0.2
2.7	1.5	0.5	0.2
2.7	1.3	6	0.1
2.7	0.8	18	0.1
2.7	0.3	42	<0.2

As part of the Evansville, IN, project, the performance of a 545-m^3/day (100-gpm) pilot plant using source water chlorination followed by chlorine dioxide disinfection was compared with that of the full-scale plant using chlorination only.[63] This comparison using the full-scale plant as a control was performed after a 2-week study showed that equivalent amounts of trihalomethanes were produced in both plants when a sufficient free chlorine residual was maintained through filtration, thus indicating that the control was valid. As shown in Table 57, little InstTTHM was formed with chlorine dioxide addition in the pilot plant (note that the chlorine dioxide contained an average of 9.5 percent free chlorine). But when chlorine was applied to the full-scale plant, the TTHM concentration increased from an average of 1.7 µg/L in the source water to 64 µg/L.

During the ORSANCO project, the use of chlorine dioxide was investigated at the Hays Mine Plant of the Western Pennsylvania Water Company.[18] At this location, the chlorine dioxide was generated by adding hydrochloric acid to sodium chlorite (Figure 106). Because chlorine is not involved in the reaction, a nearly chlorine-free chlorine dioxide solution was produced. The chlorine dioxide dose to the source water was 1.5 mg/L, which did not exceed the disinfectant demand, as chlorine dioxide was not found in the coagulation-clarification basin effluent. The significant decrease in InstTTHM concentration that occurred when the source water disinfectant was switched from chlorine to chlorine dioxide is shown in Figure 107 (page 180).

Chlorine dioxide has been widely used in Europe as an alternative to chlorine for drinking water disinfection for some time.[141] Although these operations are considered successful with regard to disinfection, control of trihalomethanes through the use of chlorine dioxide disinfection has not been well documented in most places. Several examples are given here, however, to demonstrate that the USEPA findings reported above are borne out by others.

For example, Hamilton, OH, has been using chlorine dioxide for disinfection for at least the last 6 years.[142] Here, the finished water contained less than 1 µg/L of InstTTHM, and the 2-day TermTTHM, measured with 5 mg/L of chlorine added, was 16 µg/L. Although the trihalomethane precursor concentration in this water was low, the use of chlorine dioxide has avoided the production of significant quantities of trihalomethanes.

TABLE 56. INFLUENCE OF A MIXTURE OF CHLORINE DIOXIDE AND CHLORINE ON TRIHALOMETHANE PRODUCTION IN OHIO RIVER WATER[39]

Test reaction time, hr	ClO_2		Cl_2		Control (Cl_2 only) residual, mg/L	ClO_2/Cl_2 ratio	TTHM, µg/L	% TTHM reduction*
	Dose, mg/L	Residual, mg/L	Dose, mg/L	Residual, mg/L				
23	0.5	T†	2.0	0.3	0.8	0.25	54	20
48	0.7	0.3	2.3	1.2	0.6	0.31	30	23
25	0.5	0.2	1.4	0.4	0.3	0.33	26	48
42	1.9	0.5	4.1	2.4	1.9	0.46	41	40
22	1.3	0.6	1.5	0.2	0.05	0.87	25	60
24	2.0	0.4	2.0	0.7	0.8	1.0	28	59
38.5	2.2	0.3	2.0	0.6	0.4	1.1	29	49
27	4.2	3.2	2.5	1.6	1.0	1.7	6	84
27	4.2	2.3	2.5	1.5	1.0	1.7	8	80
24	1.8	1.3	0.9	0.4	0.1	1.9	6	84
50	4.7	2.7	2.0	0.5	0.4	2.4	5.3	93
21	3.5	3.1	0.8	0.4	T	4.3	1.6	96
24	2.8	1.8	0.5	NR‡	T	5.6	<0.1	100

*Compared with a chlorine-only control where the chlorine dose is equal to the chlorine dose in the test system.

†Trace.

‡Not run.

TABLE 57. USE OF CHLORINE DIOXIDE FOR TRIHALOMETHANE CONTROL IN OHIO RIVER WATER AT EVANSVILLE, IN[63]

Date, 1979	InstTTHM, μg/L		
	Raw water influent	Full-scale plant effluent, Cl_2 treatment only*	Pilot plant effluent, Cl_2 and ClO_2 treatment†
9/18	0.9	109	1.2
9/25	6.1‡	84	3.0
10/2	0.3	95	2.9
10/9	0.5	82	0.7
10/16	0.3	84	1.2
10/23	0.1	36	0.8
10/30	0.4	53	0.9
11/14	0.6	51	1.2
11/20	0.5	40	1.3
11/27	0.4	46	1.2
12/4	9.9‡	42	5.9
12/11	0.2	41	0.8
Avg.	1.7	64	1.8

*Average applied Cl_2 dose to raw water = 6.3 mg/L.
Average residual Cl_2 in full-scale plant effluent = 1.7 mg/L.
†Average applied ClO_2 dose to raw water = 1.5 mg/L.
Average residual ClO_2 in pilot plant effluent = 0.3 mg/L.
‡Reason these values were higher than normally found is not known.

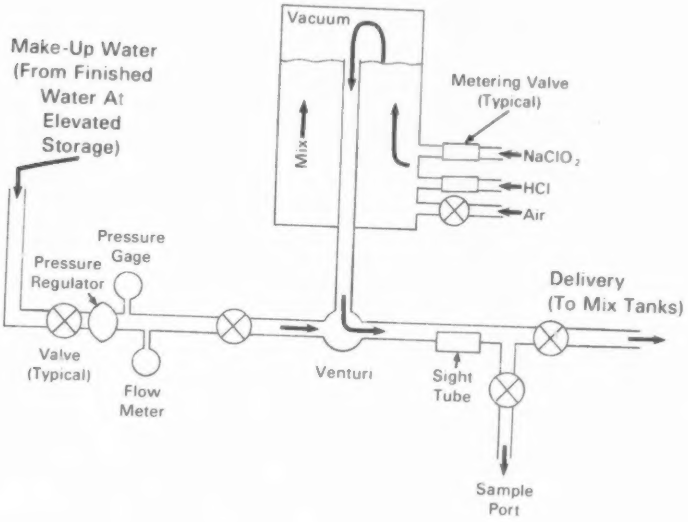
Make-Up Water (From Finished Water At Elevated Storage)
Vacuum
Mix
Metering Valve (Typical)
NaClO₂
HCl
Air
Pressure Gage
Pressure Regulator
Delivery (To Mix Tanks)
Valve (Typical)
Flow Meter
Venturi
Sight Tube
Sample Port

Figure 106. ORENCO (Rio Linda Chemical Co., Rio Linda, CA) chlorine dioxide generator used at the Western Pennsylvania Water Company, Pittsburgh, PA.[18]

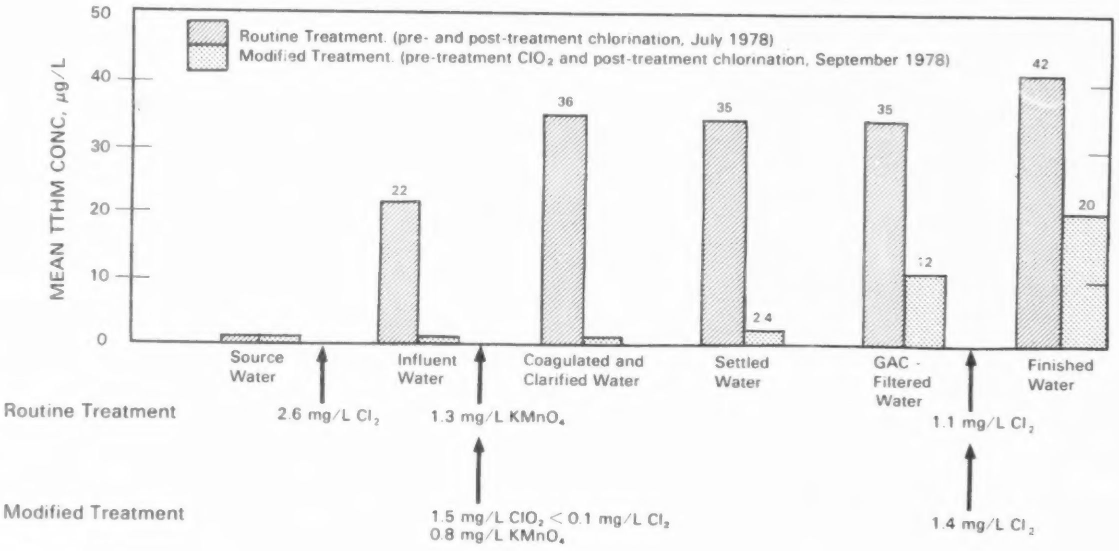

Figure 107. Mean TTHM concentration in water given routine (Cl_2 only) and modified (ClO_2 and Cl_2) treatment at the Pennsylvania water company, Pittsburgh, PA. (45,000-m^3/day [12-mgd capacity].)[18]

The Louisville Water Company has also performed some experiments with chlorine dioxide as an alternative disinfectant (a companion to the studies with combined chlorine reported earlier in this section under Chloramines).[135] In this case, the addition of ammonia was included in the treatment process to combine with any free chlorine that might remain in the water as a result of the generation of the chlorine dioxide. Note that chlorine dioxide does not react with ammonia. Specifically, 0.6 to 0.8 mg/L of chlorine dioxide was added to the coagulation basin effluent, and 0.5 mg/L of ammonia was added to the softening basin influent. At this utility, softening follows coagulation-sedimentation. Under this treatment scheme, the InstTTHM concentration in the distribution system was less than 5 $\mu g/L$. If needed, this treatment may be used in the summer months.

Several reports have appeared recently in which various utilities have investigated the use of chlorine dioxide in place of chlorine as the primary disinfectant. These data (Table 58) show the same pattern as reported in the in-house USEPA studies and the four case histories presented above. Both in the laboratory and in the field, the use of chlorine dioxide clearly can reduce the resulting TTHM formation when compared with equivalent free chlorination.

TABLE 58. TTHM's PRODUCED IN TREATMENT, WATER DISINFECTED WITH CHLORINE DIOXIDE

Location	InstTTHM with free chlorine, $\mu g/L$	InstTTHM with ClO_2, $\mu g/L$	Reference
Shreveport, LA	68	1.2	111
Davenport, IA	152	62	66
Peoria, IL	60	6	66
Bethesda, OH	284	16	Personal communication*
Contra Costa, CA	>100	None	20

*J. Lucas, USEPA, 1980.

Ozone—In a previously unpublished in-house USEPA study on the possibility of trihalomethane formation during ozonation, a 3.7-cm (1.5-in) diameter glass counter-flow contact chamber with a fritted glass sparger was used. Ohio River water was ozonated at 2 different doses, and the trihalomethanes produced were compared with those of a control in which chlorine was used as the disinfectant. The data in Table 59 show that virtually no trihalomethanes were formed during the ozonation experiments. Consideration was given to the possibility that the ozone might oxidize either chloride or bromide or both to active chlorine or bromine species and thereby produce trihalomethanes during ozonation. But the data in Table 59 indicate no such occurrence.

TABLE 59. EFFECT OF OZONATION ON TRIHALOMETHANE PRODUCTION IN OHIO RIVER WATER, CONTINUOUS-FLOW STUDIES

Applied ozone dose, mg/L*	Chlorine dose, mg/L	Trihalomethanes, $\mu g/L$			TTHM, $\mu g/L$
		$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	
0.7	0	0.2	NF†	NF	0.2
0	8	6	14	4	24
18.6	0	0.2	NF	NF	0.2
0	8	12	9	2	23

*O_3 contact time = 5 to 6 minutes.
†None found.

The data collected during the study cited in Reference 141 show that more than 1000 water utilities in Europe use ozone as the primary disinfectant. Although bromoform may be formed under unusual conditions of high bromide content,[143] the USEPA in-house studies show clearly that ozonation does not cause formation of trihalomethanes under normal drinking water treatment conditions. Therefore, even though the trihalomethane content is not known for most of these European utilities, trihalomethanes should not be formed at these plants as a result of ozonation. The Strasburg, PA, water utility used ozone as the only disinfectant and was the only utility in the National Organics Reconnaissance Survey that did not have measurable quantities of trihalomethanes in the finished water.[7] In this case, however, comparisons are difficult, because the TermTHM concentration was not determined on this water.

Bromine Chloride—When free chlorine was used as a disinfectant in an in-house USEPA study (Table 60), the primary trihalomethane was chloroform; but when bromine chloride was used as a disinfectant, almost all of the trihalomethane content appeared as bromoform, with hypobromous acid probably being the primary reactive hydrolysis product of bromine chloride.[36] Furthermore, more TTHM's were formed when bromine chloride rather than free chlorine was used as the disinfectant (Figure 108). Thus these data indicate that the use of bromine chloride is not necessarily desirable because of the formation of large quantities of bromine-containing trihalomethanes, mostly bromoform.

TABLE 60. TRIHALOMETHANE FORMATION IN TREATMENT, WATER DISINFECTED WITH CHLORINE AND BROMINE CHLORIDE[36]

Reaction time, hr	Trihalomethanes formed with Cl_2, µg/L				Trihalomethanes formed with $BrCl_2$, µg/L			
	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$
6	44	16	3.4	0.2	0.3	<0.1	1.7	149
24	85	23	4.5	1.3	0.4	<0.1	2.0	177
48	106	28	5.2	0.3	0.5	0.1	2.7	194
72	116	30	5.8	0.2	0.6	0.2	3.2	209
96	118	41	5.9	0.3	0.5	0.1	3.4	209

Iodine—The formation of trihalomethanes during iodination was studied by Rickabaugh and Kinman.[144] Examples of their findings (Table 61) show that none of the regulated trihalomethanes[3] were formed when iodine was used as the disinfectant. Nonetheless, some iodoform (CHI_3) was probably formed, but because an analysis was not made, the quantity is unknown. Furthermore, because some dichloroiodomethane was formed, diiodochloromethane was probably also formed. Therefore, whether or not a true reduction in trihalomethane production occurred cannot be determined from this study. Finally, the USEPA position is that iodine should be used only in emergency situations or for transient populations because of possible toxicity problems.[145]

Disinfection Byproducts Other Than Trihalomethanes—

When disinfectants (oxidants) are used in water treatment, byproducts other than the trihalomethanes may be formed. This subsection attempts to summarize the information currently available on this specific subject. For further information see Reference 146.

For purposes of comparison, the subject of other disinfectant byproducts is introduced with a summary of the available information regarding chlorination byproducts other than trihalomethanes, followed by a corresponding discussion for each alternate disinfectant (chlorine dioxide, chloramines, and ozone).

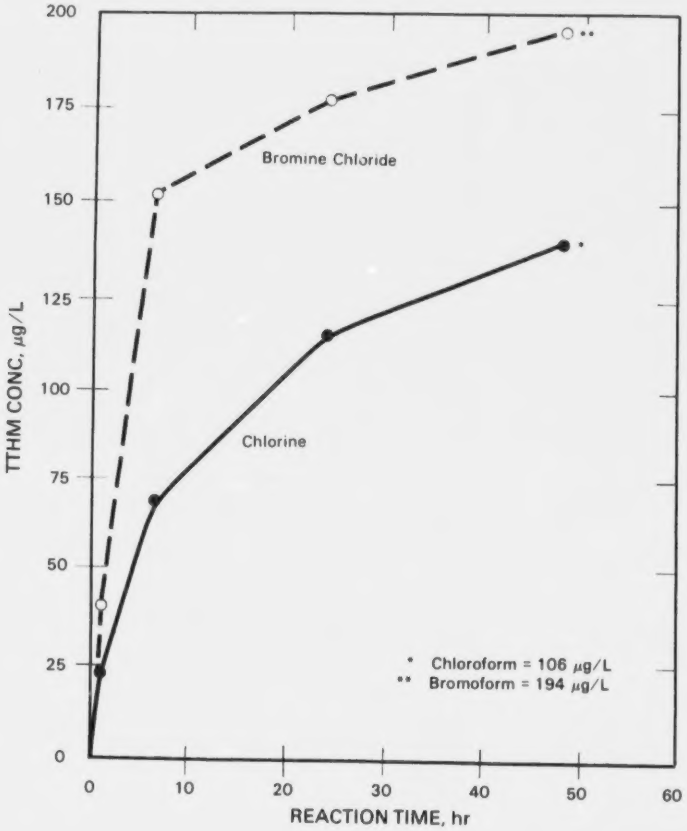

Figure 108. Formation of trihalomethanes during water treatment using free chlorine and bromine chloride as disinfectants.[36]

Chlorine—Nonpolar compounds other than trihalomethanes that were either not detectable in the source water or were present in lower concentrations have been detected in finished water at ng/L to μg/L concentrations. Most of the sources of these are poorly understood. At least 19 nontrihalomethane, halogenated, volatile compounds were found by Rook[21] in the Rotterdam Storage Reservoir. Stieglitz et al. found additional compounds formed at low concentrations in a Rhine River bank filtrate sample upon chlorination.[147] Rook speculated on a possible pathway to explain the formation of some of the observed byproducts as related to his proposed mechanism for trihalomethane formation from *m*-dihydroxyphenyl moieties.

TABLE 61. FORMATION OF TRIHALOMETHANES DURING WATER TREATMENT USING IODINE AND CHLORINE AS THE DISINFECTANT*[144]

Disinfectant	Dose, mg/L	Residual, mg/L	Trihalomethanes, μg/L						TTHM, μMol/L
			$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	$CHICl_2$	CHBrClI	
Free chlorine	10.0	1.68	156	27	34	NF†	NF	NA‡	1.64
Iodine	10.0	1.15	NF	NF	NF	NF	36	NF	0.17

*pH, 8.0; temperature, 25°C (77°F); reaction time, 24 hours.

†None found.

‡Not analyzed.

Stieglitz suggested no mechanism. Coleman et al. reported the co-presence of chloropicrin, chlorobenzene, a chlorotoluene isomer, and a chloroxylene isomer as well as their respective logical precursors (nitromethane, benzene, toluene, and *m*-xylene) in finished chlorinated tap water.[148] With the exception of benzene, all of the above precursors were shown to react with free chlorine to form the expected products.

In later studies at the USEPA laboratory (unpublished data, 1978) chloroacetonitrile derivatives were observed in a finished tap water. Concentrations of acetonitrile in the mg/L range could not be made to react with free chlorine under realistic reaction conditions to form detectable chlorinated derivatives. But Trehy showed that dichloro-, bromochloro- and dibromoacetonitrile were formed upon low pH chlorination of a south Florida drinking water source.[149] At high pH, such as in lime softening systems these byproducts are not formed or are later destroyed. In addition, in-house work by USEPA in cooperation with Manchester, NH, has shown the formation of dichloro- and 1,1,1-trichloroacetone upon chlorination.[103] Suffet et al. previously found 1,1,1-trichloroacetone in two tap waters, but not in the respective source waters.[150]

Furthermore, even simple aromatic hydrocarbons have been observed in some studies to be more prevalent or in higher concentrations in finished tap water than in the respective raw source water.[151,152] With regard to some hydrocarbons, subsequent in-house USEPA studies have shown that biodegradation of these compounds during sample transit and storage are important considerations and may have occurred to a greater extent in the undisinfected source water samples than in the chlorinated finished water samples. The result would be an apparent increase in compound concentration in the finished water when little or no increase had actually occurred.

The best known reactions of free chlorine with aromatic compounds in the water treatment field are those that occur with phenols.[153] Chlorine reacts rapidly with phenol to form mono-, di-, and tri-chloro derivatives. These compounds are highly odorous and are slowly decomposed by excess chlorine. Other phenolics and substituted aromatics can also be chlorinated.[154]

Samples collected by USEPA at eight utilities show that significant concentrations of halogenated disinfection byproducts other than the trihalomethanes (as measured by the organic halogen test[70]) are formed in many cases, and that the ratio of nontrihalomethane halogenated byproducts to the trihalomethanes varies from location to location (Table 62).[36]

Chlorine Dioxide—Organic Byproducts—Although chlorine dioxide does not react to produce trihalomethanes, considerable evidence indicates that chlorine dioxide does react with organic material during water treatment and, like chlorine, is therefore likely to produce other organic byproducts. Specific observations about this likelihood are as follow:

1. Because chlorine dioxide is a good disinfectant, some reaction does take place between the cell components of the organism and the chlorine dioxide.
2. Even though chlorine dioxide does not react with ammonia, most waters exhibit a chlorine dioxide demand similar to (but somewhat less than) that of chlorine (Figure 109).
3. At applied chlorine dioxide concentrations higher than those encountered in drinking water treatment, identifiable byproducts have been isolated.[155]
4. Chlorine dioxide destroys phenolic compounds when the oxidant is used for taste and odor control in water supplies.[120]
5. Most important, as shown in Section VII, Subsection Oxidation (Chlorine Dioxide), the presence of chlorine dioxide reduces the formation of trihalomethanes by chlorine. This and other evidence obtained by Miltner indicated that chlorine

dioxide reacts with natural humic acids.[39] Such information is not surprising, because chlorine dioxide is effective for reducing the concentration of color in drinking water supplies.[156]

The possible formation of organic byproducts arising from the use of chlorine dioxide as a disinfectant in drinking water was first considered by USEPA on the basis of the existing literature. An in-house laboratory study followed to determine the validity of extrapolations from the literature that described work where concentrations of oxidant and organic materials were generally high.

As a result, a brief review of the literature considered pertinent to drinking water applications was presented by Stevens et al.,[157] although a much more extensive and complete review of chlorine dioxide chemistry is available elsewhere.[155] Briefly, the literature describes chlorinated and nonchlorinated derivatives (including acids, epoxides, quinones, aldehydes, disulfides, and sulfonic acids) that are products of reactions carried out under conditions somewhat different from those experienced at water treatment plants.

TABLE 62. ORGANIC HALOGEN (OX) IN FINISHED WATERS*[36]

Utility	Nonpurgeable OX (NPOX)† concentration, μg/L as Cl⁻	Purgeable OX (POX) (mostly TTHM) μg/L as Cl⁻	NPOX/POX Ratio
A	17	9.8	1.7
B	NF‡	NF	—
C	52	64	0.8
D	36	31	1.2
E	165	180	0.9
F	136	114	1.2
G	66	133	0.5
H	98	27	3.6

*Raw waters did not contain OX.

†NPOX = The concentration of organic halogen that remains in a sample after it has been purged for a trihalomethane analysis.

‡None found.

Nonetheless, because of the potential for undesirable byproduct formation resulting from chlorine dioxide disinfection of drinking water, an in-house investigation was begun at the USEPA laboratory to determine if byproducts of the type predicted by the literature (where reactions described were carried out at generally higher concentrations) would prevail under drinking water disinfecting conditions. This work was carried out in two phases:

1. A search of gas chromatographic data for differences in purgeable compounds found in chlorine-dioxide-treated and untreated waters, and
2. Development and use of a more elaborate analytic scheme to detect products of a more diverse nature, specifically those expected from reactions of phenolic compounds.

The semiquantitative results of the first phase have been briefly described in the literature where C_2 through C_8 aldehydes were noted to increase in concentration after treatment of a natural water with chlorine dioxide.[157] In that work, no other dramatic differences were observed between treated and untreated samples with regard to compounds amenable to the purge-and-trap[3] type of chromatographic analysis used.[7,29,148]

Phenol was selected as the model compound for the beginning of the second phase, primarily because of the supposed polyphenolic nature of humic materials (trihalomethane precursors that make up a large fraction of the organic material present in natural waters where trihalomethane formation is a problem) (Figure 110).[158] Table 63 presents the results of one experiment where phenol was exposed to varying molar ratios of ClO_2 to phenol.

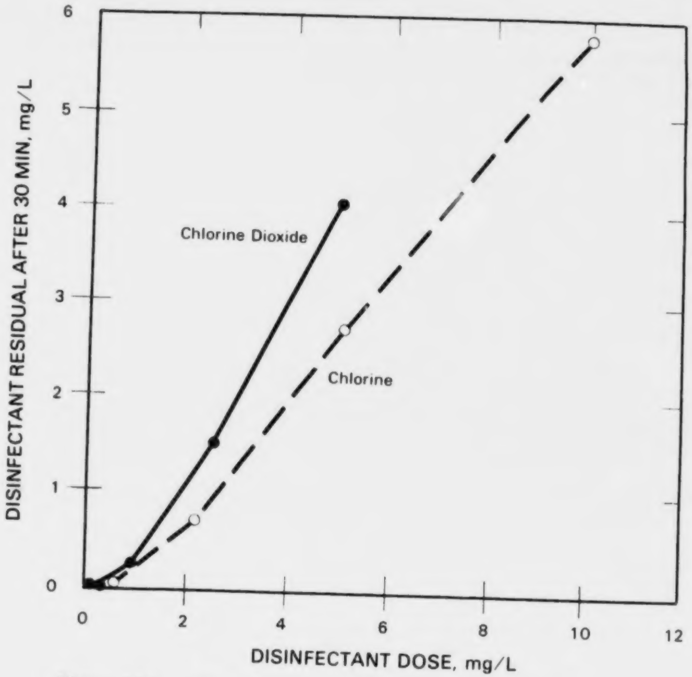

Figure 109. Comparison of disinfectant demands for Ohio River water, November 17, 1975. pH 7.5; 23 ntu; standard plate count 10,000/mL; total coliform density 700/100 mL.[36]

The data in Table 63 show that chlorophenols were produced at low molar ratios (4/5) of chlorine dioxide to phenol. Higher ratios (14/5 and 14/1) did not produce chlorophenols, but they did favor hydroquinone formation. This effect was expected to some extent, based on the literature,[157,159-161] even though odorous chlorophenolic materials are avoided in drinking water through the use of chlorine dioxide.[120] Other expected organic byproducts such as oxalic and maleic acids, and 2,6- and 2,5-dichloro-*p*-benzoquinone were not immediately identifiable, although total organic carbon concentration data indicate that the phenol is not completely converted to carbon dioxide. To date, no gas chromatographable compounds in this category that were not present in the untreated sample have been identified in chlorine-dioxide-treated natural waters or in humic- and fulvic acid solutions. Note that detection limits were estimated to be in the range of 5 to 10 μg/L as phenol.

The finding of individual identifiable species from the chlorine dioxide treatment was not necessarily expected because of the polymeric nature of the natural humic material in contrast to the monomeric phenol model. To investigate the possible formation of higher molecular weight chlorinated species that could not be identified by gas chromatographic techniques, humic acid was added to chlorine dioxide at two different chlorine dioxide to carbon (ClO_2/C) ratios. To compare yields of organic halogen, two reaction ratios with corresponding electron equivalents to chlorine were included in the experiment. That is, the molar ratios 1/15 and 1/3 selected for ClO_2/C correspond to the molar ratios 1/3 and 5/3, respectively, selected for

Cl_2/C (Table 64). The basis for this correspondence is that chlorine dioxide going to chloride requires 5 electrons per chlorine atom, whereas chlorine going to chloride requires only one electron per chlorine atom.

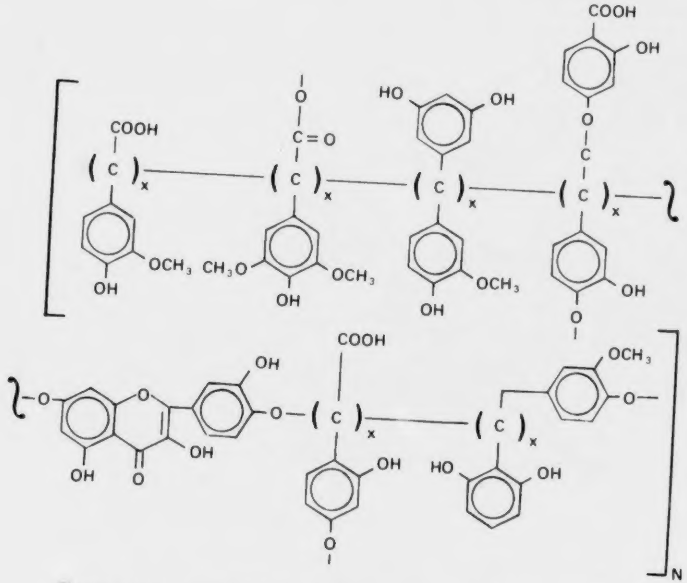

Figure 110. A proposed humic structure.[158] (Adapted from JOURNAL American Water Works Association, Volume 58, No. 6 [June 1966] by permission. Copyright 1966, the American Water Works Association.)

TABLE 63. PRODUCTS RESULTING FROM CHLORINE DIOXIDE TREATMENT OF PHENOL

ClO_2/phenol† mol/mol	Percent yield from phenol*					
	o-chloro-phenol	phenol (recovered)	2,4-dichloro-phenol	p-chloro-phenol	p-hydro-quinone	Total recovery
4/5	11	30	0.3	13	3.6	58
14/5	NF‡	NF	NF	NF	7.2	7.2
14/1	NF	NF	NF	NF	45	45

*Reaction time = 4 hours.
†In mg/L: 4/5 = 43.5/75, 14/5 = 150/75, and 14/1 = 164/16.
‡None found.

According to the chlorination data (Table 64), the organic halogen yield is much higher than the chloroform yield for the 1-hour reaction time and increases with chlorine dose, the chloroform concentration remaining essentially constant. Chlorine dioxide produced some (but less) organic halogen and, as expected, an insignificant concentration of chloroform. The trend toward less halogen substitution at the higher ClO_2/C ratio, observed with phenol reactions, was not observed here; however, this interpretation is complicated by the longer reaction time that was allowed at the higher chlorine dioxide dose. Factors influencing organic halogen yields relative to trihalomethanes from all disinfectants are now under investigation in the USEPA laboratory.

TABLE 64. REACTION OF HUMIC ACID WITH CHLORINE AND CHLORINE DIOXIDE

Oxidant/C ratio, mol/mol	Cl_2,ClO_2 doses, mg/L	Reaction time, hr	$CHCl_3$, μg/L	OX, μg/L as Cl^-
Cl_2/C:				
1/3	3.8	1	39	198
5/3	19.4	1	32	278
ClO_2/C:				
1/15	0.75	1	0.4	23
1/3	3.7	2	1.6	52.5

Inorganic Byproducts—As noted above, when chlorine dioxide reacts with organic compounds to oxidize them, the byproduct chlorite (ClO_2^-) is formed. Furthermore, as chlorine dioxide disproportionates in water, both chlorite and chlorate (ClO_3^-) are formed as byproducts. The relative proportion of these byproducts was determined during a USEPA in-house study in which 1.5 mg/L of chlorine dioxide was added to Ohio River water that had been treated in a pilot plant.[162] The data in Table 65 show that approximately 50 percent of the original chlorine dioxide was converted to chlorite, about 25 percent to chlorate, and approximately 25 percent to chloride.[162] Thus when chlorine dioxide is used as an alternative disinfectant, the health significance of inorganic anions other than chloride (the sole major inorganic byproduct of chlorine treatment) must be considered. These inorganic byproducts are unique to chlorine dioxide.

TABLE 65. INORGANIC CHLORINE DIOXIDE BYPRODUCTS*[162]

	Initial concentration,		Final concentration,		Percent ClO_2 demand
Species	mg/L	mg/L as Cl^-	mg/L	mg/L as Cl^-	
ClO_2	1.5	0.8	0	0.1	—
ClO_2^-	—	—	0.7	0.4	50
ClO_3^-	—	—	0.4	0.2	25
Cl^-	17.9	17.9	18.1	18.1	25
Total	—	18.7	—	18.7	100

*1.5 mg/L ClO_2 added to coagulated, settled, dual-media filtered Ohio River water. Reaction time = 42 hours; pH = 7.1.

Chloramines—The potential for formation of organic byproducts as a result of disinfection with chloramines is not as obvious as with chlorine dioxide. Chloramines are weaker disinfectants (less reactive with cells) compared with chlorine and chlorine dioxide, and waters generally exhibit a much lower disinfectant demand when chloramines are used. Because chloramines do hydrolyze to form traces of free chlorine (see Subsection Disinfectant Chemistry Effects earlier in this section), some reaction products of this oxidant might be expected, but at much lower concentrations in a given time than when free chlorination is practiced. Except for chlorine exchange reactions with primary and secondary amines present in treated waters, information regarding specific byproduct formation from chloramines under drinking water treatment conditions is virtually absent from the literature.[163]

Sontheimer, reporting on research performed at Stuttgart, Federal Republic of Germany, showed that chloramines do produce some organic halogen when they are used as the disinfectant, although the concentration is considerably lower than that produced when free chlorine is the disinfectant[140] (Table 66).

TABLE 66. ORGANIC HALOGEN FORMATION IN DRINKING WATER AT STUTTGART, FEDERAL REPUBLIC OF GERMANY[140]

Type of treatment and water	Dissolved organic chlorine µg/L as Cl⁻
With breakpoint chlorination:	
River	50
Sedimentation basin effluent	640
With combined chlorine residual:	
River water	23
Sedimentation basin effluent	72

Ozone—Ozone is a highly reactive oxidant that might be expected to produce oxidation products of organic materials found in water supplies. Unlike the oxidants chlorine, chlorine dioxide, and chloramines, however, ozone would not be expected to produce chlorinated byproducts.

Although much is known about ozone reactions in other media, surprisingly little information exists about the action of ozone as an oxidant of organic compounds in aqueous solution. This lack of data exists even though ozone has been in widespread use for decades as a water and wastewater disinfectant. The sum of knowledge in this area is summarized in a recent National Academy of Science Literature Review.[163] This document suggests that oxygenated products such as ketones, aldehydes, and acids are most likely formed from alcohols and olefinic double-bond and aromatic ring cleavage.

Of the few studies performed in connection with drinking water treatment, a study by Schalekamp is the most revealing concerning byproduct formation.[164] Schalekamp analyzed water before and after an ozone treatment step at various ozone doses. He found that the concentration of total aldehydes and ketones rose by a factor of more than 10 as the ozone dose increased from 0 to 5 mg/L and declined slightly when the ozone dose was changed from 5 to 7 mg/L. The data in Table 67 show the increases in specific aldehydes during these studies (note that the concentrations are in nanograms per liter).

Sievers et al. also found the same aldehydes and reported some apparent hydrocarbon formation upon ozonation of the effluent from a secondary waste treatment plant in Estes Park, CO.[165] To date, no other studies of actual in-plant treatment byproducts have been reported.

Summary—Individual Compounds—The following is a quotation [illegible]m the conclusion of National Academy of Sciences review of the literature on disinfection byproducts for the USEPA.[163]

Nonetheless, it is clear that each disinfectant chemical that was examined in this survey produces by-products that may occur in actual water treatment applications. Of particular concern are the following substances that result from the use of the various disinfectants.

- From chlorine: the trihalomethanes (THM's), trichloroacetone (CCl_3COCH_3), and other largely uncharacterized chlorinated and oxidized intermediates that are formed from the complex set of precursors in natural waters; chloramines; chlorophenols; and the largely unknown products of dechlorination.
- From ozone: epoxides which may in principle result from unsaturated substrates such as oleic acid, although none have yet been found in drinking water; peroxides and other highly oxidized intermediates such as glyoxal (OHCCHO) and methyglyoxal (CH_3COCHO) from aromatic precursors.
- From bromine and iodine: THM's and other bromine and iodine analogs of chlorinated species; bromophenols, bromoindoles, and bromoanisoles; plus the halogens themselves, which may remain in drinking water as residual.
- From chlorine dioxide: chlorinated aromatic compounds; chlorate (ClO_3^-) and chlorite (ClO_2^-) which are often present as by-product or unreacted starting material from production of chloride dioxide; and chlorine dioxide itself.

This list, incomplete as it is, is compelling in that it shows that each disinfectant produces chemical side effects that should be examined in more detail before the disinfectant is widely adopted for water treatment. It is clear that each of these disinfectants, being highly reactive chemical agents, will have inevitable side effects.

Organic Halogen—Two in-house USEPA studies compared the formation of organic halogen when four different disinfectants were used. In these experiments, Ohio River water that had been coagulated, settled, and filtered in the pilot plant was disinfected with free chlorine, chloramines, chlorine dioxide, and ozone. The resulting samples were then analyzed for organic halogen. For this experiment, these data show that organic halogen is formed by the action of these disinfectants in the following order of yield (Table 68):

free chlorine > chloramines > chlorine dioxide > ozone

In this case, the disinfectant dose varied among samples and was adjusted (except O_3) to be roughly equivalent to the 2-day disinfectant demand. In Test 1, the OX was approximately 1/4 trihalomethanes and in Test 2, 1/10 trihalomethanes; trihalomethane formation was insignificant for the other disinfectants. Under circumstances where the disinfectant dose was equivalent among the tests, the order of organic halogen production might change. Ozone formed no organic halogen in either test when compared with the no-disinfectant control. The chlorine dioxide data confirmed the findings presented in Table 64.

Although information on byproducts other than trihalomethanes from disinfection is currently limited, the data presented here indicate that sufficient evidence is available to show that these byproducts certainly do occur. Furthermore, although the health effects have not yet been evaluated, research is under way in an attempt to provide this information.[71,146,166,167] Although these byproducts are not currently regulated, water purveyors should make every effort to minimize their concentration in finished drinking water.

Discussion

The data presented in Section VIII indicate that none of the three alternative disinfectants investigated extensively—chloramines, chlorine dioxide, or ozone—will react with humic acids or other precursor materials to produce significant concentrations of trihalomethanes. This conclusion was reached first in the laboratory and then verified with many case histories of actual experiences on the treatment-plant scale. Nonetheless, the use of disinfectants other than free chlorine to control trihalomethanes has advantages and disadvantages, which are discussed in the following subsection.

TABLE 67. FORMATION OF ALDEHYDES IN WATER TREATED WITH VARIOUS OZONE DOSES AT THE LENGG WATERWORKS[164]

(ng/L)

Aldehyde	Ozone dose, mg/L							
	1		2.5		5		7	
	Before O_3	After O_3	Before O_3	After O_3	Before O_3	After O_3	Before O_3	After O_3
Hexanal	NF*	40	NF	78	NF	74	NF	24
Heptanal	8	82	30	140	18	145	20	68
Octanal	6	74	22	190	16	320	26	110
Nonanal	7	160	34	340	26	680	55	164
Decanal	12	260	36	240	38	920	80	134
Undecanal	NF	40	NF	64	NF	82	26	16
Dodecanal	NF	28	16	24	NF	58	24	12
Tridecanal	NF	NF	NF	12	NF	24	20	8
Tetradecanal	12	26	10	6	NF	30	20	4

*None found.

TABLE 68. FORMATION OF ORGANIC HALOGEN (OX) IN OHIO RIVER WATER TREATED WITH VARIOUS DISINFECTANTS

(μg/L as Cl^-)

	Free chlorine	Chloramines	Chlorine dioxide	Ozone	No disinfectant (control)
Test 1	194(2.5 mg/L)*	101(2.0 mg/L)	61(3.0 mg/L)	9(3.0 mg/L)	17
Test 2	53(3.3 mg/L)	26(0.8 mg/L)	17(2.4 mg/L)	11(1.0 mg/L)	13

*Disinfectant dose is indicated in parentheses.

Summary of Advantages and Disadvantages to Using Alternative Disinfectants for Trihalomethane Control

Advantages of Using Alternative Disinfectants—

The major advantage to using alternative disinfectants is the ability to lower trihalomethane concentrations near detection limits in most cases through the use of any of the three alternative disinfectants studied (chlorine dioxide, chloramines [combined chlorine], or ozone). Furthermore, two of the alternative disinfectants, chloramines and chlorine dioxide, can readily be prepared and fed at a water treatment plant, although careful attention is needed to maintain a low concentration of chlorine in the chlorine dioxide. In addition, worldwide experience with the use of all three of these disinfectants already exists, giving water treatment plant designers and operators confidence in their use. Finally, two of the alternative disinfectants, chlorine dioxide and ozone, are excellent disinfectants and their disinfecting power is consistent over the pH range usually encountered in water treatment; the third, combined chlorine, is a weaker disinfectant, but it is adequate in many cases.

Disadvantages of Using Alternative Disinfectants—

The major disadvantage to using alternative disinfectants as a technique for controlling trihalomethane concentrations is that because they are themselves oxidants, they will produce other organic byproducts unless the organic content of the water is lowered. This disadvantage is analogous to the removal of trihalomethanes themselves (such as by aeration) after they are formed by chlorination. Little evidence exists at the present time to indicate whether the byproducts of the alternate disinfectants are more or less safe to consumers than the non-trihalomethane byproducts of chlorination.

Thus, although the trihalomethane concentration of the finished water is improved, the overall water quality may not be equally improved because the health hazard of the organic byproducts that may be formed has yet to be completely evaluated.[71,146,166,167] Additionally, each of the disinfectants itself has inherent disadvantages; for example, ozone does not produce a residual for the distribution system, chloramine is a weaker disinfectant than free chlorine and may itself have some toxicity,[168] and chlorine dioxide produces chlorite and chlorate as inorganic byproducts—anionic species whose health effect is currently unknown.[71,146] (Because of the potential toxicity of chlorite and chlorate, the USEPA has *recommended* in the Trihalomethane Regulation[1] that the total residual concentrations of chlorine dioxide, chlorite, and chlorate be limited to 0.5 mg/L in drinking water).

Finally, water is used for many purposes in a community—industrial, medical, and nonpotable domestic uses such as houseplants, tropical fish, and so forth. Thus, any change in the chemical makeup of drinking water, such as a change in disinfectant, may cause some problems in the community. For example, chloramines cause difficulty to kidney patients using dialysis machines[169] and can cause problems to those raising tropical fish (L. Harms, South Dakota School of Mines and Technology, 1979, and P. Lassovszky, USEPA, Washington, D.C., 1980, personal communications).

SECTION IX
MAINTAINING BACTERIOLOGIC QUALITY

Background

The microbial barrier concept in the treatment of drinking water is of particular importance in the processing of unprotected surface waters laden with a variety of sewage inputs, stormwater, and animal waste discharges. Groundwater may also become contaminated with seepages of landfill leachates, migration of organisms from land application of sewage effluents, or movement of wastes in sewage lagoon basins through ground faults to the aquifers below. All of these sources of pollution often contain pathogenic bacteria, viruses, yeasts, and multicellular parasites.

Effective water treatment has had a major impact on the reduction of waterborne disease. Where waterborne disease outbreaks have occurred, deficiencies in treatment (particularly filter breakthrough and inadequate or interrupted disinfection) have been major causes of the problem. For this reason, maintaining the integrity of the treatment barrier is essential as treatment changes are made to meet the requirements of the Trihalomethane Regulation[1] (see Sections VI–VIII).

The treatment changes most likely to alter the transport and fate of microorganisms within the treatment chain involve: 1) lowering the trihalomethane concentration by changing the point of chlorination to follow clarification (see Section VII, Subsection Clarification), 2) organic chemical removal by biologic activity during GAC adsorption (see Section VII, Subsection Biologic Degradation), and 3) changes in types of disinfectant and disinfectant application (see Section VIII). This section discusses the impact of these treatment processes on the bacteriologic quality of finished water and, where possible, the influence on the bacteriologic quality of distributed water.

Removal of Trihalomethane Precursors

Clarification—Changing Point of Chlorine Application—

Although the primary reason for the use of disinfectants in potable water treatment is to kill or inactivate pathogenic organisms that may be present, source water chlorination has often been used for a variety of other reasons:

1. To oxidize hydrogen sulfide and similar objectionable compounds in source water,
2. To improve coagulation of waters containing iron and manganese,
3. To aid in maintenance of filtration sand beds by preventing slime growths, algal formation, and other organic deposits, and
4. To limit microbial populations applied to filters, thereby enabling more uniform efficiency in bacterial reduction in that part of the treatment chain.

As can be seen from several of these benefits for source water chlorination, locating the point of chlorine application near the end of the treatment chain could impose an increased burden on coagulation, filtration, and clarification to perpetuate a high level of microbial reduction in the processed water. In two full-scale field evaluations of a change in the chlorine application point from source water to clarified water, variation in the water utility source waters and clarification processes resulted in two different in-plant conditions.[18,170]

The Pittsburgh, PA, Department of Water routinely chlorinated untreated Allegheny River water. Water quality data representative of 2 weeks of sampling during routine treatment and 2 weeks of sampling during modified treatment are presented in Table 69. These data indicate that chlorination of source water before clarification resulted in a reduction of the mean total coliform density from 6,200 organisms/100 mL in the source water to <1 total coliform/100 mL in the clarified water. The modified treatment scheme produced a similar reduction of the source water total coliform population (from 6,300 organisms/100 mL to <1 organism/100 mL) before the application of chlorine. With this scheme, coagulation and settling combined with the application of PAC for taste and odor control and approximately 1 mg/L potassium permanganate for manganese control during clarification and before chlorine application were as effective in coliform reduction as source water chlorination and clarification combined. Some evidence of a delay in the reduction of standard plate count until after chlorine application did, however, occur.

Changing the point of chlorine application was also studied at the Cincinnati Water Works (OH) in a series of 2-week study periods.[18] During routine treatment plant operation, chlorine was applied to the source water after 48 hours of open reservoir storage. Adequate retention time of source water is in itself a beneficial first step in microbial population reduction through self-purification processes; it is also a buffer against temporary impairment of water quality from some accidental upstream spill of industrial chemicals. In the Cincinnati water treatment operation, coagulant is added to the open reservoir, and chlorine is routinely applied ahead of in-plant treatment processes. The modified chlorine application took place after an additional 4-hour clarification process consisting of coagulation and settling.

The results of both the routine and modified treatment schemes show that 48-hour source water storage with alum treatment reduced the total coliform densities by approximately 97 percent, and the turbidities by approximately 90 percent (Table 70).[18,170] The coagulation and settling process, however, had little effect on further turbidity reductions, and further reduction of the coliform population was only about 50 percent. Locating the point of chlorination after coagulation and settling resulted in an intrusion of coliforms into the early stages of water treatment and placed increased importance on maintaining an effective disinfection process at this stage to reduce the burden on filtration. The apparent persistence of a residual standard plate count into the filtration stage, regardless of the point of disinfection, illustrates the chlorine-resistant nature of some of these organisms. In either event, neither a measurable change in the bacterial quality of the finished water, nor any apparent in-plant problems developed as a result of the modified treatment scheme.

Granular Activated Carbon Adsorption—

Coliform and Standard Plate Count Organisms—In the adsorption of organic substances, including those that may be trihalomethane precursors, GAC particles become focal points for bacterial nutrients and also provide suitable attachment sites for microbial habitation. Although the portion of organic removal in this process, possibly attributable to biodegradation, is small compared with physical adsorption to the activated carbon surface, a substantial microbial population develops at the water-activated carbon surface interfaces. This process can therefore be of microbiologic concern in that treatment barriers must remain effective against increased bacterial population densities that can include regrowth of indicators and selective adaptation by some organisms that are disinfectant-resistant, opportunistic pathogens, or known antagonists to coliform detection. As a result of these concerns, the bacteriologic conditions associated with virgin GAC placement and full-scale use in the sand replacement mode were evaluated at two utilities.[18]

A pilot-scale investigation of GAC adsorption was conducted at the Huntington Water Corp., Huntington, WV. A single bed of virgin WVW 14x40 GAC, selected for its history of effective taste and odor control, was evaluated for trihalomethane control and for its effect on microbiologic densities. A 0.8-m (2.5-ft) layer of GAC

TABLE 69. CHLORINE APPLICATION POINT STUDY USING ALLEGHENY RIVER SOURCE WATER AT THE PITTSBURGH, PA, DEPARTMENT OF WATER[18,170]

	Mean value at various sample points*									
	Cl_2 application to source water†					Cl_2 application to clarified water‡				
Parameter	Source water	Clarified water	Settled water	Filtered water	Finished water	Source water	Clarified water	Settled water	Filtered water	Finished water
Flow time, hr	0	2	15	16	32	0	2	15	16	32
Turbidity, ntu	7.2	0.84	0.58	0.04	0.04	7.1	1.0	0.9	0.05	0.02
Total coliforms/ per 100 mL	6,200	<1	<1	<1	<1	6,300	<1	<1	<1	<1
Standard plate count/mL	§	31	3	3	4	§	230	5	<1	<1
pH	7.1	8.8	8.8	8.8	8.0	7.1	8.8	8.8	8.8	8.2
Free Cl_2 residual, mg/L	§	0.2	0.2	0.1	0.1	§	<0.1**	0.3	0.1	<0.1
Total Cl_2 residual, mg/L	§	0.6	0.3	0.3	0.2	§	0.2**	0.6	0.4	0.2
		↑			↑			↑		↑
		Cl_2 application, 1.2 mg/L			Cl_2 application, 2.4 mg/L			Cl_2 application, 0.5 mg/L		Cl_2 application, 2.7 mg/L

*Two-week sample period, seven samples.
†Source water temperature = 24°C (75°F).
‡Source water temperature = 21°C (70°F).
§Not run.
**MnO_4^- interference in amperometric determination of chlorine.

TABLE 70. CHLORINE APPLICATION POINT STUDY USING OHIO RIVER SOURCE WATER AT THE CINCINNATI, OH, WATER WORKS[18,170]

	Mean value at various sample points*									
	Cl_2 application to source water stored 48 hr and treated with alum†					Cl_2 application to coagulated and settled water‡				
Parameter	Source water	Stored source water	Coagulated and settled water	Filtered water	Finished water	Source water	Stored source water	Coagulated and settled water	Filtered water	Finished water
Flow time, hr	0	48	52	52.5	55.5	0	48	52	52.5	55.5
Turbidity, ntu	32	1.0	1.2	0.11	0.10	14	0.80	1.1	0.07	0.06
Total coliforms/ 100 mL	9,600	200	<1	<1	<1	84,000	2,400	1,400	<1	<1
Standard plate count/mL	§	§	500	<1	5	§	§	5,500	15	<1
pH	7.3	7.0	8.5	8.3	8.7	7.6	7.2	8.1	8.1	8.2
Free Cl_2 residual, mg/L	§	§	1.8	1.6	1.5	§	§	0	1.8	1.4
Total Cl_2 residual, mg/L	§	§	2.0	1.8	1.6	§	§	0	2.0	1.5
			↑ Cl_2 application, 3.6 mg/L					↑ Cl_2 application, 3.3 mg/L		

*Two-week sample period, seven samples.

†Source water temperature = 24°C (75°F).

‡Source water temperature = 22°C (72°F).

§Not run.

was placed on top of 0.3 m (1 ft) of sand and gravel and then backwashed several times to remove fine particles. When the bed was placed in operation, it received water that had been chlorinated, coagulated, and settled. The flow through the bed represented only 8 percent of the flow through the entire plant.

Results of this investigation are summarized in Table 71. The mean total coliform density in the source water during the 32-week study period was 3,400 organisms/100 mL. Following chlorination, coagulation, and settling, the total coliform density in the influent to the GAC bed was found to be <1 coliform/100 mL at the time of sampling. The standard plate count in this water (aside from one indeterminant high value) ranged from 4 to 55 organisms/mL. On passing through the activated carbon filter/adsorber, some deterioration in the bacterial quality occurred during the first 9 weeks of operation, when warm water conditions prevailed. At that time, 1 to 8 total coliforms/100 mL were found in the GAC filter/adsorber effluent, but this occurrence was not accompanied by a significant increase in the standard plate count. No correlations with turbidities or peak total coliform loadings could be made. Note that GAC treatment did consistently reduce turbidity.

These data suggest that total coliforms did occasionally break through early treatment stages, which included chlorination, but because of the infrequent sampling, they were not detected in the activated carbon filter/adsorber influent. Although these total coliform occurrences could not be related to one or more breaks in the early stages of the treatment barrier, the data do indicate that coliforms may persist for some time or possibly multiply in an activated carbon filter/adsorber bed provided with inflows of warm water. Although not shown in Table 71, application of chlorine following the GAC filtration/adsorption was found to be adequate in maintaining a finished water quality of <1 total coliform/100 mL and a standard plate count below 500 organisms/mL in this water treatment system.

When the Beaver Falls, PA, Municipal Authority replaced three of its eight sand filters (sand replacement mode) with GAC for full-scale taste and odor control, a concurrent evaluation for trihalomethane control and bacteriologic conditions was conducted.[18] Three different activated carbons were used: Filtrasorb® 400, Filtrasorb® C,* and HD 8 × 16. Source water from the Beaver River was treated with coagulant, settled, then mixed with lime and chlorine and settled again before filtration. Potassium permanganate was not routinely applied to the water until the 21st week and beyond, when breakpoint chlorination was stopped. Note the low free chlorine residual values for this period (Table 72).

This preliminary treatment during the 32-week study period was sufficient to reduce total coliform densities ranging from 6,000 to 220,000 organisms/100 mL in the source water to densities in the settled GAC influent that were generally undetectable in 100 mL of sample (Table 72).[18,170] One weekly sample contained 2 coliforms/100 mL. Two other samples contained 1 coliform/100 mL in the influent water to the activated carbon filter/adsorber beds. A comparison of the data on total coliform bacteria (Table 72) shows that coliforms in the activated carbon filter/adsorber effluents were in excess of influent densities during the first 12 weeks of filter/adsorber operations. Here again, warm water temperature appeared to be the critical factor, because by week 13, when the source water temperature had declined to 4°C (39°F), total coliforms became undetectable in 100 mL. A significant drop in the activated carbon filter/adsorber effluent standard plate count densities from all three beds occurred as the source water temperature declined below 10°C (50°F).

Because of the apparent correlation between bacterial densities in GAC effluents and source water temperatures, additional bacteriologic sampling was done when the source water temperatures were again above 10°C (50°F). Data presented in Table 73 verified the initial observations that effluent total coliform densities from

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*Not commercially available.

TABLE 71. GAC STUDY USING OHIO RIVER SOURCE WATER AT THE HUNTINGTON, WV, WATER WORKS[18]

Week	Source water			GAC influent (chlorinated, coagulated, settled water)					GAC effluent (WVW 14x40)				
	Temperature, °C	Turbidity, ntu	Total coliforms/100 mL	Residual chlorine, mg/L		Turbidity, ntu	Total coliforms/100 mL	Standard plate count/mL	Residual chlorine, mg/L		Turbidity, ntu	Total coliforms/100 mL	Standard plate count/mL
				Free	Total				Free	Total			
1	27	14	1,600	0.8	1.4	2.0	<1	4	0	0	0.21	<1	100
2	28	21	1,200	0.3	0.4	4.6	<1	52	0	*	1.5	<1	53
3	28	26	910	1.8	3.7	4.9	<1	42	0.1	0.3	1.4	6	12
4	28	13	870	0.5	0.7	4.4	<1	7	*	0.3	1.7	8	41
5	28	15	1,500	0.6	0.9	6.5	<1	18	0.4	0.6	1.8	5	18
6	27	80	3,000	0.5	0.8	5.8	<1	28	0.1	0.2	1.1	<1	13
7	26	37	5,300	0.4	0.7	3.8	<1	17	*	0.1	0.54	<1	3
8	27	34	2,300	0.3	0.6	5.9	<1	22	0.2	0.4	1.5	2	25
9	27	17	1,400	0.5	0.7	3.3	<1	24	*	0.2	0.27	2	46
10	27	18	970	0.5	0.7	4.6	<1	26	*	0.2	3.2	<1	140
11	26	25	1,100	0.4	0.6	7.9	<1	28	*	0.2	1.7	<1	23
12	24	24	1,700	0.5	0.7	4.4	<1	28	*	*	0.36	1	12
13	19	47	3,100	0.5	0.8	8.7	<1	31	*	0.2	0.42	<1	30
14	19	98	4,300	0.5	0.9	4.3	<1	†	0.1	0.4	0.44	<1	†
15	14	34	3,900	0.5	0.7	16	<1	34	†	†	0.44	<1	2
16	15	22	2,600	0.5	0.9	9.1	<1	39	*	0.5	0.97	<1	10
17	15	18	3,000	0.4	0.9	10	<1	18	*	0.6	0.47	<1	2
20	11	42	3,900	0.6	0.8	5.5	<1	>200	0.3	0.4	0.65	<1	4
22	8	240	1,400	0.2	0.3	9.8	<1	55	0.2	0.4	12	<1	11
23	5	160	26,000	0.5	0.6	8.0	<1	36	0.2	0.3	0.78	<1	3
25	3	24	2,800	0	0.7	7.0	<1	30	0	0.5	0.50	<1	<1
27	2	30	5,900	0.9	1.1	9.0	<1	†	0.3	0.5	0.15	<1	†
32	2	34	610	0.3	0.9	14	<1	†	0.4	0.8	0.34	<1	†

*Trace.
†Not run.

TABLE 72. GAC STUDY USING BEAVER RIVER SOURCE WATER AT THE BEAVER FALLS, PA, MUNICIPAL AUTHORITY[18,170]

	Source water			GAC influent					GAC effluent**														
									Filtrasorb® 400				Filtrasorb® C*				HD 8x16						
Week	Temperature, °C	Turbidity, ntu	Total coliforms/100 mL	Residual chlorine, mg/L Free	Residual chlorine, mg/L Total	Turbidity, ntu	Total coliforms/100 mL	Standard plate count/mL	Residual chlorine, mg/L Free	Residual chlorine, mg/L Total	Total coliforms/100 mL	Standard plate count/mL	Residual chlorine, mg/L Free	Residual chlorine, mg/L Total	Total coliforms/100 mL	Standard plate count/mL	Residual chlorine, mg/L Free	Residual chlorine, mg/L Total	Total coliforms/100 mL	Standard plate count/mL			
1	21	44	98,000	2.0	†	5.6	<1	†	0	0	64	†	0	0	85	†	0	0	46	†			
2	21	28	71,000	1.7	1.7	4.8	<1	†	0	0	75	†	0	0	95	†	0	0	25	†			
3	15	22	140,000	1.3	1.4	2.3	<1	†	0	0	98	1,000	0	0	130	740	0	0	33	1.700			
4	11	9.5	150,000	1.1	1.3	2.9	<1	100	0	0	45	1,400	0	0	50	60,000	0	0	23	1,100			
5	16	7.5	39,000	1.2	1.4	2.5	<1	800	0	0	34	25,000	0	0	28	42,000	0	0	12	3,800			
6	16	9	190,000	1.4	1.6	3.3	<1	350	‡	<0.1	42	2,000	‡	<0.1	12	40,000	0.1	0.2	13	3,000			
7	16	10	80,000	1.1	1.2	3.6	<1	10	‡	<0.1	28	20,000	‡	<0.1	12	52,000	‡	<0.1	2	45,000			
8	10	9	98,000	1.0	1.0	3.2	<1	42	‡	<0.1	22	29,000	‡	<0.1	21	32,000	‡	<0.1	8	92,000			
9	10	16	220,000	1.3	1.6	4.6	2	110	‡	‡	13	6,500	‡	<0.1	7	6,500	‡	<0.1	2	21,000			
10	8	10	120,000	1.0	1.3	4.5	<1	33	‡	<0.1	12	1,600	‡	<0.1	18	1,800	‡	<0.1	5	1,800			
11	6	14	120,000	1.4	1.6	3.7	<1	95	‡	<0.1	2	960	‡	<0.1	1	820	‡	<0.1	1	900			
12	3	10	69,000	1.0	1.1	5.9	1	360	‡	<0.1	1	270	‡	<0.1	2	380	‡	<0.1	<1	320			
13	4	22	89,000	1.2	1.7	4.6	<1	660	‡	<0.1	<1	480	‡	<0.1	1	540	‡	<0.1	<1	380			
14	2	10	75,000	1.3	1.5	6.6	1	200	‡	‡	1	440	‡	<0.1	<1	110	‡	<0.1	<1	200			
15	1	10	65,000	1.0	1.2	4.8	<1	120	‡	<0.1	<1	44	‡	<0.1	<1	50	‡	<0.1	<1	74			
17	1	12	48,000	1.4	1.7	5.9	<1	150	‡	<0.1	<1	50	‡	<0.1	<1	16	‡	0.1	<1	26			
18	1	8	27,000	1.0	1.1	5.5	<1	33	‡	<0.1	<1	21	‡	<0.1	<1	20	‡	<0.1	<1	9			
22	1	14	6,000	0.4	1.6	6.4	<1	30	‡	0.3	<1	30	‡	0.4	<1	23	<0.1	0.4	<1	47			
23	4	10	23,000	0.3	1.6	5.8	<1	24	‡	0.4	<1	13	‡	0.2	<1	10	‡	0.4	<1	15			
25	4	150	84,000	‡	1.4	6.6	<1	38	‡	0.2	<1	21	‡	0.2	<1	35	‡	0.2	<1	24			
27	7	12	13,000	†	1.4	6.3	<1	58	†	0.1	<1	41	†	0.1	<1	27	†	0.2	<1	10			
29	10	8	24,000	0.2	1.1	1.7	<1	33	†	0.1	<1	31	†	0.1	<1	28	†	0.3	<1	17			
32	11	6	8,400	0.2	1.6	1.9	<1	17	†	0.3	<1	69	†	0.2	<1	82	†	0.3	<1	19			

*Not commercially available.

†Not run.

‡Trace.

**Turbidity in the three GAC media effluents was below 1 ntu.

TABLE 73. RESULTS OF ADDITIONAL SAMPLING DURING GAC STUDY USING BEAVER RIVER SOURCE WATER AT BEAVER FALLS, PA, MUNICIPAL AUTHORITY[18,170]

	Source water		GAC influent		GAC effluent					
					Filtrasorb® 400		Filtrasorb® C*		HD 8x16	
Week	Temperature, °C	Total coliforms/ 100 mL	Free chlorine residual, mg/L	Total coliforms/ 100 mL	Free chlorine residual, mg/L	Total coliforms/ 100 mL	Free chlorine residual, mg/L	Total coliforms/ 100 mL	Free chlorine residual, mg/L	Total coliforms/ 100 mL
53	26	18,000	1.4	<1	†	100	†	64	†	130
54	23	10,000	1.2	<1	†	120	†	25	†	240
55	22	22,000	1.6	<1	†	230	†	21	†	730
56	19	9,200	1.6	<1	†	470	†	5	†	330
57	14	31,000	1.4	<1	†	62	†	9	†	82
58	12	10,000	1.1	<1	†	44	†	10	†	55
59	14	8,700	1.4	<1	†	30	†	3	†	31
60	13	19,000	1.3	<1	†	8	†	<1	†	9
61	11	5,000	1.5	<1	†	‡	†	2	†	<1
62	9	12,000	0.8	<1	†	1	†	<1	†	<1
63	8	82,000	1.2	<1	†	<1	†	<1	†	<1
64	6	8,000	1.0	<1	†	<1	†	<1	†	<1

*Not commercially available.
†Trace.
‡Not run.

all three activated carbon filter/adsorber beds exceeded influent densities of <1 organism/100 mL when temperatures were above 10°C (50°F). When the temperature again dropped below 10°C (50°F), effluent total coliform densities returned to below detectable levels in 100 mL. High initial total coliform occurrences may also be attributed to the difficulty of disinfecting adsorption beds when putting them into service. These field data confirmed the similar observation from the Huntington, WV, study (Table 71). They also suggest that occasional coliform penetration past the early stages of treatment and before filtration can occur, and that these organisms *may* become temporarily established in the activated carbon filter/adsorber effluent.

Both coliform and standard plate count density increases during GAC treatment were much more pronounced at Beaver Falls, PA, than at Huntington, WV. Higher levels of total coliform contamination in the source water for Beaver Falls also suggest that nutrient levels in that source water may have been higher. This condition would tend to support growth in GAC adsorbers. No TOC data were available, but the THMFP was somewhat higher at Beaver Falls than at Huntington. THMFP declined as temperature and organic concentrations also dropped. These changes contributed to a parallel recession in the bacterial population. The variability in results observed at these two plants points up the need for close monitoring wherever GAC adsorption is employed as a treatment process. The increased coliform and standard plate count density occurring during GAC treatment place a critical importance on maintaining an effective disinfectant barrier following GAC filtration/adsorption. Because of final disinfection, finished water bacteriologic quality at Beaver Falls, PA, was adequately maintained during the entire study period, with a total coliform density of <1 organism/100 mL and a standard plate count density below 500 organisms/mL.

Bacterial Populations in Granular Activated Carbon (GAC) Adsorbers—The bacterial population that develops in activated carbon adsorbers (both in the sand replacement and post-filter mode) includes (1) a specialized group of organisms capable of biodegrading organics adsorbed from the source water and (2) those bacterial survivors passing through the early stages of the water treatment train. Included in studies by the Philadelphia Water Department (Torresdale facility) on activated carbon adsorber designs for better organics removal was routine monitoring for total coliforms and general bacterial populations.[110] Although this investigation is still in progress, available data confirm the recovery of several coliforms, including *Citrobacter freundii, Enterobacter cloacae, Klebsiella pneumonia,* and *K. oxytoca.*

Furthermore, GAC adsorbers showed approximately a 10- to 100-fold increase in the general bacterial populations, compared with control systems, when the influent was ozonated. This stimulation of bacterial growth on GAC adsorbers is presumably caused by the oxidative breakdown of some organics by ozone treatment, which results in more usable organics for bacterial metabolism. Pilot-plant studies (see Section VII, Subsection Biologic Degradation) confirm that the number of bacteria in the activated carbon adsorber effluent after ozonation of the influent waters remains significantly higher than if the influent waters were simply aerated (that is, passed through the contact chamber unexposed to ozone). As a result, bacteria *may* eventually penetrate the adsorber in large enough numbers to challenge the disinfection barrier.

The Philadelphia study also included examinations for *Actinomycetes* and fungi. Limited available information on these microbial contributors to taste and odor suggest that colonizations *may* occur in activated carbon adsorbers and sand filters, but at an apparently lower density than encountered in the source water.[110]

The bacterial flora of activated carbon adsorption and sand filter beds, the bacterial quality of adsorber and filter effluents, and the effects of disinfection on the organisms colonized in a model treatment process have been studied by Parsons.[171]

Results of this investigation indicated that a variety of bacteria in a groundwater source survive lime softening and colonize downstream in sand filters or activated carbon adsorbers. The size and composition of the bacterial population within these filters will: 1) change more with seasonal temperatures than with treatment processes or operations of the system, 2) vary with the chemical quality of the influent water, and 3) possibly form slime that may interfere with bed maintenance by preventing adequate backwashing and that may slough off large numbers of organisms into the system effluents.

Population profiles of bacteria released from activated carbon adsorbers and sand filters used to treat unchlorinated groundwater were investigated at Miami, FL.[171,172] Dominant organisms in the effluent from aged GAC adsorbers and sand filters were: *Pseudomonas, Moraxella, Acinetobacter, Alcaligenes,* gram positive bacilli, and unidentified organisms. During the USEPA in-house study, bacterial profiles obtained from dual-media filters receiving either nonozonated or ozonated water revealed that the exposure to ozone caused a more selective bacterial population to be released in the effluent (J. Caruthers, Spelman College, personal communication 1979). Profiles of dominant organisms present in the influent and effluent of dual-media filters receiving ozonated and nonozonated source water are shown in Figures 111 through 113. Note that although similar types of dominant organisms were encountered in these studies, bacterial survivors of ozonation were greatly restricted in species diversity. This change in bacterial flora composition in turn stimulated a significant increase in the bacterial density of ozonated effluent. Among the recessive strains encountered (i.e., a broad spectrum of bacteria with less than 5 percent occurrence) were a variety of pigmented organisms that became established in the adsorbers and found their way into the effluent. Although the significance of these organisms is uncertain, they appear frequently in drinking water and possibly may colonize GAC adsorbers and sand filter beds.

A study of pigmented organisms in the activated carbon adsorbers at Evansville, IN, also revealed a periodic colonization (D. Reasoner, USEPA, personal communication 1980). Both virgin GAC and reactivated carbon adsorber effluents contained some pigmented bacteria, even though the influent to the GAC adsorber sometimes showed no significant pigmented bacterial population during periods when increased concentrations of chlorine dioxide were applied to the untreated river water (Table 74). Apparently, disinfectant residuals during May-December 1979 were inadequate to be an effective, controlling force in the GAC adsorbers. No disinfectant residuals were detected in these GAC adsorber effluents because of specific oxidant/GAC reactions. Analyses during March-April 1980, however, showed a few pigmented bacteria in the source water and essentially none from the GAC adsorber (these data are not included in Table 74). This change may have been caused by a drastic seasonal decline in the occurrence of these bacteria in the source water, or it may have resulted from the more effective (higher dose) application of chlorine dioxide to the source water to maintain a residual of 0.3 to 0.5 mg/L chlorine dioxide in the GAC adsorber influent.

One of the areas of greatest confusion in studying changes in the bacterial population and speciation of organisms in GAC adsorbers has been the selection of a culture protocol (including medium, incubation, time, and temperature) to optimize recovery and identification of these organisms. The standard plate count procedure (SPC agar, 35°C [95°F] incubation for 48 hours) measures that portion of the total bacterial population related to coliform interference, opportunistic pathogens, and effectiveness of chlorine residuals.[173,174] This procedure probably does not, however, adequately detect either the magnitude of bacterial growth in adsorber beds or the full extent of regrowth within the distribution system.

Investigation of the problem reveals the need to use a medium with a variety of nutrients in low concentrations, such as R-2A medium.[175] Increasing the length of the incubation time at a lower temperature—28°C (82°F)—further enhances the recovery of organisms that may be present in the GAC adsorbers. Table 75 illustrates

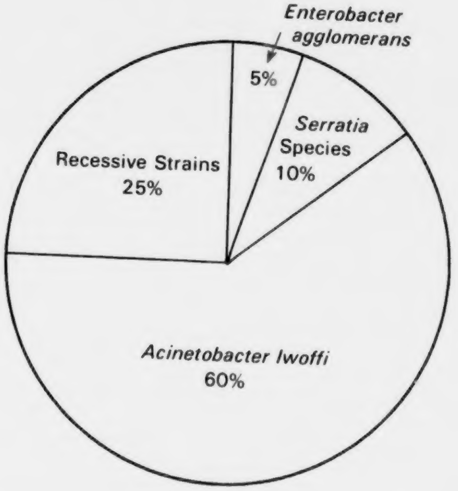

Figure 111. Profile of dominant organisms present in influent of a dual-media filter receiving nonozonated source water. (Average specific plate count of 5,500 organisms/mL).

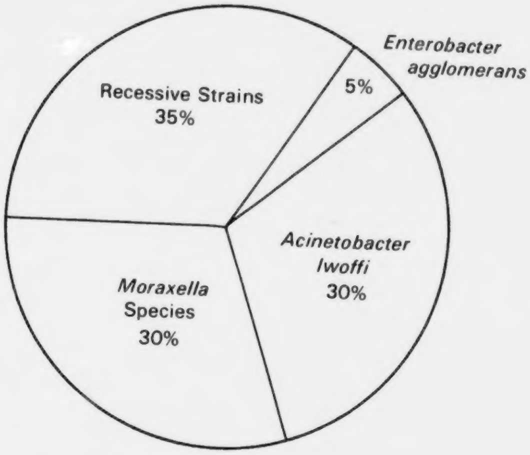

Figure 112. Profile of dominant organisms present in effluent of a dual-media filter receiving nonozonated source water. (Average specific plate count of 3,900 organisms/mL.)

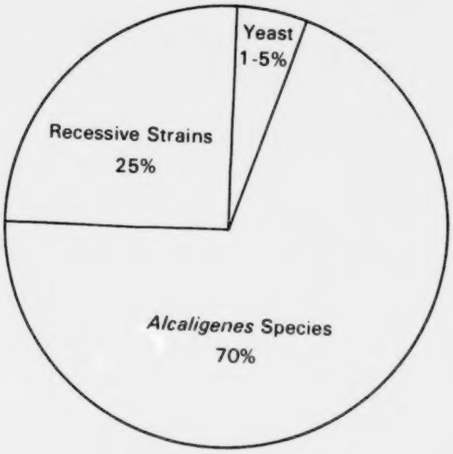

Figure 113. Profile of dominant organisms present in effluent of a dual-media filter receiving ozonated source water. (Average specific plate count of 36,000 organisms/mL.)

TABLE 74. PERCENT OCCURRENCE OF PIGMENTED BACTERIA IN GAC FILTER EFFLUENTS FROM CHLORINE-DIOXIDE-TREATED OHIO RIVER WATER[*,†]

Sample date (1979)	Coagulated, settled, filtered water		Virgin activated carbon effluent		Reactivated carbon effluent	
	ClO_2 residual, mg/L	Percent pigmented bacteria	ClO_2 residual, mg/L	Percent pigmented bacteria	ClO_2 residual, mg/L	Percent pigmented bacteria
May 15	0.3	94	<0.1	0.3	<0.1	2
May 29	0.1	68	<0.1	8	<0.1	4
June 12	0.2	90	<0.1	25	<0.1	7
June 26	1.0	27	<0.1	11	<0.1	2
July 10	0.5	None	<0.1	12	<0.1	7
July 24	0.6	None	<0.1	27	<0.1	13
Oct 9	0.3	88	<0.1	46	<0.1	36
Oct 23	0.2	82	<0.1	22	<0.1	25
Nov 22	0.6	None	<0.1	36	<0.1	19
Dec 4	0.5	None	<0.1	41	<0.1	21

[*] Pigmented bacteria occurrences determined from colony counts obtained on SPC agar (35°C [95°F] incubation for 7 days).

[†] D. Reasoner, USEPA, Personal communication, 1980.

TABLE 75. BACTERIAL POPULATIONS IN WATER TREATMENT PROCESSES USING STANDARD PLATE COUNT MEDIUM OR R-2A MEDIUM WITH EXTENDED INCUBATION TIMES*,175
(Organisms/mL)

Sampling day	Source water			Lime-softened water			Sand filter effluent			GAC adsorber effluent		
	SPC,† 2 days‡	SPC, 6 days§	R-2A, 6 days	SPC, 2 days	SPC, 6 days	R-2A, 6 days	SPC, 2 days	SPC, 6 days	R-2A, 6 days	SPC, 2 days	SPC, 6 days	R-2A, 6 days
Initial	110	300	470	120	350	510	890	1,200	1,500	<1	140	220
7	<1	14	43	31	202	510	820	22,000	35,000	1	25,000	95,000
14	4	2	13	7	7	130	<1	1,200	9,400	<1	600	4,400
21	<1	2	43	7	18	150	2,200	2,500	33,000	<1	5,200	16,000
28	<1	<1	28	3	39	530	700	7,800	67,000	1	11,000	55,000
35	<1	2	10	<1	490	330	100	6,000	25,000	<1	12,000	74,000
42	10	11	3	70	120	1,700	1,200	71,000	22,700	**	56,000	52,000
49	3	11	15	9	1,200	23	5,000	41,000	3,000	80	4,200	100
56	8	21	84	<1	10	<1	<1	700	12,000	**	1,900	50,000
63	2	25	200	29	190	3,000	170	2,000	3,000	**	5,000	48,000

*All cultures incubated at 35°C (95°F).
†Standard plate count.
‡Standard plate count incubation time.
§Extended incubation time.
**Not run.

recovery data for organisms found in several different stages of drinking water treatment processes using two different media and extending the incubation time to 6 days for the standard plate count procedure.

Accurate location of the sites where bacterial colonization occurs in a GAC adsorber and the determination of the magnitude of the bacterial population have presented two difficult problems in analyses that may account for conflicting results and conclusions derived from the research literature. In a recent study, Parsons found that shaking exposed GAC in buffered dilution water was not adequate for removal of adhering bacteria.[172] Furthermore, grinding in a blender or tissue grinder was also inadequate because of some cell disruption, reattachment of bacteria to a newly created activated carbon surface, or simultaneous settling of bacterial cells with activated carbon particles. Highest density recovery of bacteria from GAC particles was obtained with sonication—20-kilohertz, 180-watt output for 4 minutes (Table 76). Sites for intense bacterial colonization in GAC adsorbers appear to vary with the adsorber bed age (Table 77), bacterial species dominance, and perhaps approach (flow-through) velocity. Flow rate is probably critical because it affects nutrient transport to the microorganisms on the granular particles.[176] Though the species composition of the effluent bacteria reflected that of the bacteria established in the activated carbon adsorber, the bacterial density near the bottom of the GAC bed did not correlate with the bacterial density in the effluent (Table 77). Overall, these results suggest that bacterial growth on activated carbon particles in localized areas may be substantial and that bacteria do appear to become established in the lower part of an adsorber bed. Furthermore, these populations may pulse widely in densities, because they are a reflection of numerous variables in the adsorber column ecosystem.

Although pronounced regrowth in both the filter and adsorber beds occurred, little of this biologic activity correlated with a measurable removal of organics adsorbed on the activated carbon over a 2-month operational period (Table 78).[177] These data were developed from a comparison of TOC removed by sand filters and GAC adsorbers that received lime-softened, unchlorinated groundwater as their influent. No apparent correlation of TOC removal occurred with the age of the sand filter (63 days maximum). The data do suggest, however, that TOC removal in sand filters may be related to microbial activity, and TOC removal in GAC adsorbers of similar age may be a function of physical-chemical adsorption.

In a study on filtration-adsorption, ozonation of the influent water before application to a dual-media filter stimulated a rapid growth of organisms on the filter media (see Section VII, Subsection Biologic Degradation). This growth could have been a significant factor in the removal of organic compounds through the filter. Perhaps long-term use of sand filter beds might eventually produce a specialized population of bacteria capable of some measurable degradation of organics.

Microbial biomass concentrations were monitored at the Shreveport, LA, project where the application of extended ozone contact time for filtered water passing through several pairs of activated carbon post-filter adsorbers is being studied.[111] This investigation has produced some evidence that bacteria on activated carbon particles in these adsorbers range from 240,000 to 20 million organisms/gram of wet activated carbon by weight. Because bacterial standard plate counts in effluents reflect only a small portion of the total viable biomass established in an activated carbon adsorber, measurements of adenosine triphosphate (ATP) concentrations (a measure of metabolic energy in living cells) were also made to obtain a better total indication of all viable microbial activity.

With the use of both standard plate counts and ATP measurements, data were gathered on the source water, influent, and effluent of two GAC adsorbers in series without prior ozonation. Simultaneously, the same coagulated, settled, and filtered water was ozonated at two different detention times and then applied to other GAC adsorbers in series. Ozone contact time was the sole difference between the two ozonated waters. Results of monthly sampling demonstrated that bacterial densities

TABLE 76. RECOVERIES OF BACTERIA FROM SONICATED* OR HAND-SHAKEN GAC PARTICLES† 172

Method	Minutes processed									
	1	2	4	5	6	8	10	12	14	15
Test 1:										
Sonication	700,000	940,000	980,000	430,000	580,000	370,000	240,000	230,000	380,000	380,000
Hand shaken	14,000	—	—	—	—	—	—	—	—	—
Test 2:										
Sonication	3,300,000	4,300,000	115,000,000	2,300,000	1,500,000	700,000	400,000	1,100,000	100,000	83,000
Hand shaken	620,000	—	—	—	—	—	—	—	—	—

*Sonicator acoustic energy rated at 20 kilohertz and 180 watts maximum output.

†Shaken or sonicated in dilution water before plating (R2-A pour plates incubated at 35°C (95°F) for 12 days).

TABLE 77. BACTERIAL COUNTS* FROM TOP, MID-POINT, AND BOTTOM OF AN ACTIVATED CARBON BED AND FROM ITS EFFLUENT[172]

Column age,† days	Organisms/0.5 g dry wt‡ GAC section Top	Mid-point	Bottom	Effluent, counts/mL
6	§	58,000	55,000	250,000
11	550,000	45,000	28,000	135,000
17	130,000	4,400,000	2,700,000	30,000
20	2,790,000	460,000	320,000	44,000
25	7,700	90,000,000	50,000,000	520,000

*R2-A pour plates (35°C [95°F] incubation for 6 days).
†Ambient room temperatures.
‡Activated carbon particles sonicated for 4 minutes.
§Not run.

TABLE 78. BACTERIAL DENSITY IN SYSTEM EFFLUENTS AND PERCENT TOC REMOVAL[177]

	Sand filter effluent			GAC adsorber effluent		
Bed age, days	Bacteria,* No./mL	TOC, mg/L	Percent TOC removal	Bacteria,* No./mL	TOC, mg/L	Percent TOC removal
0	1,500	6.7	0.0	220	0.3	95.5
7	35,000	6.4	7.2	95,000	1.3	79.6
14	9,400	6.4	1.5	4,400	2.5	60.9
21	33,000	6.3	5.9	16,000	2.9	53.9
28	67,000	6.4	1.5	55,000	2.9	54.6
35	25,000	6.3	3.0	74,000	2.2	65.0
42	71,000	6.2	10.1	56,000	2.9	53.2
49	41,000	6.4	13.5	100	4.6	28.1
56	12,000	7.0	6.6	50,000	4.4	37.1
63	3,000	7.0	6.6	48,000	4.8	31.4

*R-2A medium with 35°C (95°F) incubation for 6 days.

tended to increase in GAC adsorber effluents as the temperature rose (Table 79). No positive correlation occurred between ATP concentrations and water temperature changes. Correlation of ATP concentrations with bacterial density measured by the standard plate count was inconclusive. This discrepancy occurred partly because of recovery limitations, as only a portion of the total biomass is measured in the standard plate count procedure. Furthermore, the ATP content of an average bacterium is approximately 2.5×10^{-10} μg/cell, varying among 19 species tested from 0.25 to 8.9×10^{-10} μg/cell. ATP activity must therefore be judged as a parameter on its own merit and not in relation to heterotrophic bacterial density as measured by the standard plate count of a water sample.

Essentially no change occurred in bacterial densities for nonozonated water passing through two GAC adsorbers in series. GAC influents that received prior ozonation had fewer than 10 organisms/mL, except for one test involving extended ozone contact time. In this sample, 1,500 organisms/mL were reported; yet the ATP measurement remained low, suggesting possible sample contamination during collection. All effluents from GAC adsorber pairs receiving water that had been

TABLE 79. MICROBIAL ACTIVITY IN GAC ADSORBERS RECEIVING NONOZONATED AND OZONATED WATER[111]

	Seasonal water temperature intervals											
	6.3°C (48°F)		6.9°C (44°F)		10.4°C (51°F)		13.8°C (57°F)		15.4°C (60°F)		25°C (77°F)	
Stage	BPC* No./mL	ATP† ng/L	BPC No./mL	ATP ng/L	BPC No./mL	ATP ng/L	BPC No./mL	ATP ng/L	BPC No./mL	ATP ng/L	BPC No./mL	ATP ng/L
Source	‡	886	‡	7,500	‡	3,280	‡	4,100	‡	2,520	‡	2,680
Nonozonated water:												
GAC influent	150	68	1,500	113	2,800	334	10,000	23	2,600	41	6,100	74
GAC effluent	150	50	1,100	117	3,700	335	5,000	68	2,300	49	3,100	52
Ozonated water, short detention (3 min):												
GAC influent	2	27	<1	13	<1	285	<1	13	5	27	<1	<1
GAC effluent	190	77	717	70	1,900	303	1,000	30	480	50	1,600	17
Ozonated water, long detention (40 min):												
GAC influent	5	73	<1	70	<1	303	<1	13	8	23	1,500	5
GAC effluent	90	150	490	57	1,500	300	3,500	38	15,000	68	2,400	30

*Bacterial plate count (28°C [82°F] for 7 days on soil extract agar).
†Adenosine triphosphate as a measure of metabolic activity.
‡Not run.

ozonated demonstrated a significant regrowth of organisms within the adsorber bed, reaching 10- to 1,000-fold increases over influent values. The magnitude of the regrowth was directly related to water temperature and was more intense with warm water.

Alternative Types of Disinfectants and Application Techniques

Chlorine-Ammonia Treatment (Combined Residual)—

Another approach to minimizing trihalomethane production in water treatment is to replace the free chlorine with an alternative disinfectant. Chloramines, chlorine dioxide, ozone, and ultra-violet light have been proposed as practical alternatives. Because of the desire to maintain a disinfectant residual in distributed water, chloramines and chlorine dioxide have received the most attention. Although monochloramine is definitely a less effective disinfectant than free chlorine, when compared at comparable low-dose concentrations and short contact periods (see Section VIII, Subsection Biocidal Activity) it may be practical in many plant operations where longer contact times and application of high concentrations are feasible.

Such is the case at the Jefferson Parish Water Department, Jefferson Parish, LA, where monochloramine has been relied on as the sole water disinfectant for over 30 years. In a study of data collected over an 18-month period from this water treatment plant, Brodtmann et al. reported only two total coliform occurrences in 6,720 samples of finished water.[136] This treatment system provided a 30-minute contact time before filtration, with 1.1 to 2.0 mg/L combined chlorine residual measured in the gravity sand filter effluent. Initial processing of the river source water with potassium permanganate and polyelectrolyte addition lowered the standard plate count by an average 84 percent during water clarification (Figure 114). Clarification together with 8 to 10 minutes of monochloramine contact resulted in an average 96.1 percent reduction of the source water population of standard plate count organisms. Continued processing with sand filtration in combination with a total combined residual contact time of 30 minutes lowered the initial level of measured organisms 99.7 percent. The average monthly standard plate count, reported to be below 50 organisms/ml in the distribution system, may be misleading because the problem of regrowth is generally associated with warm water temperature conditions, areas of slow flow, and dead-end sections of the distribution system. The samples measured for the monthly average were not collected exclusively under these adverse conditions.

The Louisville Water Company, Louisville, KY, was involved in a study of trihalomethane concentration control by three different disinfectant treatments.[18,178] Normal plant operations used free chlorine applied to gravity-settled source water before the clearwell. During modified treatment, ammoniation of the free chlorine residual was practiced at the clearwell during several weeks of data gathering.[18] Later in the year, application of chloramines occurred following coagulation. When ammonia was added at the softening basin, it was in some excess so that further chlorination at the clearwell would restore the chloramine residual. The net result was that a combined chlorine residual was maintained throughout the latter stages of treatment and into the distribution system.

A comparison of the bacteriologic conditions indicates that the application of chlorine to the gravity-settled source water effected a complete reduction in both total coliforms and standard plate count densities (Table 80). Densities remained low in all subsequent in-plant samples. Injecting ammonia into the clearwell at the end of the treatment train or adding ammonia in the softening basin followed by filtration and clearwell chlorination resulted in no further bacterial penetration of the treatment train. In all cases, the data demonstrated finished water of acceptable quality.

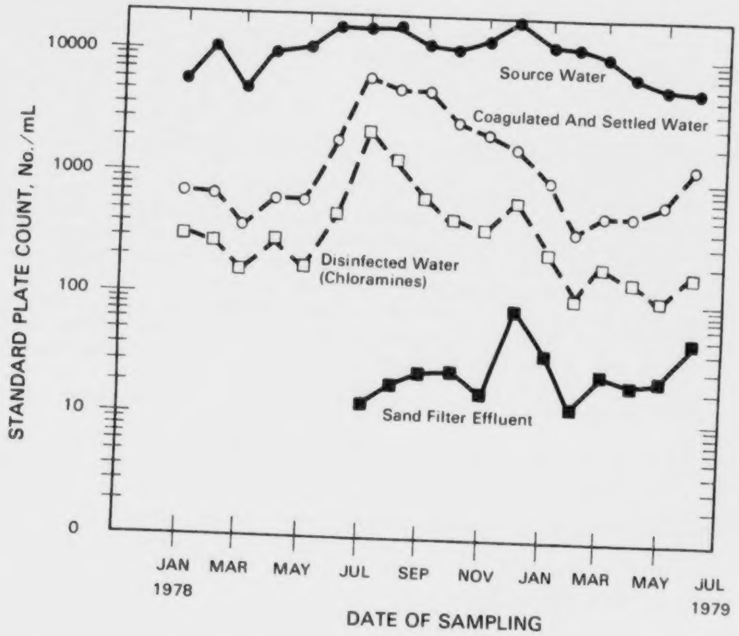

Figure 114. Standard plate count at various stages of water treatment at the Jefferson Parish Water Department (LA).[136]

Chlorine Dioxide—

Chlorine dioxide is another disinfectant that does not react with precursor materials to form trihalomethanes during water treatment (see Section VIII). The Louisville Water Company investigated the efficiency of chlorine dioxide disinfection by adding 0.6 to 0.8 mg/L chlorine dioxide at the coagulation basin effluent and applying ammonia about 10 minutes later at the influent to the next treatment step, the softening basin.[178] The chlorine dioxide residual in the softening basin effluent was usually 0.1 mg/L or less. Disinfection after filtration resulted in a combined chlorine residual of 0.8 to 1.2 mg/L, which remained unchanged throughout the 2-week chlorine dioxide study period. For comparison purposes, 2 to 3 mg/L of free chlorine was applied to the influent of the coagulation basin both before and after the study period, creating a contact time of approximately 6 hours before ammoniation.

Monitoring the standard plate count in the treatment train during both free chlorine and chlorine dioxide disinfection periods revealed a 10- to 100-fold decrease in bacterial density between the treatment plant influent water and the coagulation basin effluent. Typical values in the coagulation basin effluent were 5 to 50 organisms/mL when free chlorine was applied, and 10 to 50 organisms/mL when chlorine dioxide was added. For some unexplained reason, one high value (1,000 organisms/mL) did occur in the coagulated water early in the chlorine dioxide study, suggesting that this marginal dose of chlorine dioxide was less effective than the higher dose of free chlorine at this point in the treatment train.

TABLE 80. CHLOROMINE APPLICATION POINT STUDY USING OHIO RIVER SOURCE WATER AT THE LOUISVILLE, KY, WATER COMPANY[18,170]

Parameter	Sample point (mean values*)											
	Ammoniation at clearwell†						Ammoniation following coagulation‡					
	Source water	Settled water	Coagu-lated water	Softened water	Filtered water	Finished water	Source water	Settled water	Coagu-lated water	Softened water	Filtered water	Finished water
Turbidity, ntu	19	23	4.7	3.8	0.4	0.5	15	18	4.6	2.4	0.3	0.2
Total coliforms/ 100 mL	3,200	4,900	<1	<1	<1	<1	4,000	1,100	<1	<1	<1	<1
Fecal coliforms/ 100 mL	62	104	§	§	§	§	204	177	§	§	§	§
Standard plate count/ mL	§	§	<1	51	9	6	§	§	2.2	4	2	1
pH	7.3	7.5	7.0	9.2	9.1	8.2	7.5	7.6	7.2	9.3	9.0	8.6
Free Cl_2 residual, mg/L	§	§	2.6	0.6	0.4	0.2	§	§	1.7	§	0.1	<0.1
Total Cl_2 residual, mg/L	§	§	2.8	0.7	0.5	1.4	§	§	1.9	1.8	1.5	1.9
			↑ Chlorine			↑ Chlorine & ammonia			↑ Chlorine	↑ Ammonia		↑ Chlorine

*Based on five samples over a 9-day period.
†Source water temperature, 29°C (84°F).
‡Source water temperature, 16°C (61°F).
§Not run.

A significant increase in the general bacterial population did, however, occur in the filtered water during chlorine dioxide treatment. Standard plate count values in the filtered water were often 10 to 100 times the density observed in the coagulation basin effluent, indicating that bacterial regrowth was occurring in the filter bed. The higher bacterial densities released from the filter bed during the chlorine dioxide experiment are shown in Figure 115. This bacterial intrusion was, however, suppressed by the last treatment barrier, a secondary addition of chloramines before the clearwell. Thus the finished water quality was satisfactory.

Although concentrations of coliform bacteria were usually controlled to less than 1/100 mL upon application of either free chlorine or chlorine dioxide at the coagulation basin effluent, some significant exceptions during treatment with chlorine dioxide did occur (Figure 116). In particular, 2 to 4 coliforms/100 mL were found in the softened and filtered water, both during and after the use of chlorine dioxide. Perhaps this result could be attributed to the decreased disinfectant residuals in the softening basin effluent and the filtered water (only 0.1 mg/L of chlorine dioxide or less). No coliforms were observed, however, in any samples of the finished water before, during, or after the 2-week investigation involving chlorine dioxide and ammoniation.

The Western Pennsylvania Water Company, Hays Mine Plant, presented another opportunity to study the alternative use of chlorine dioxide as the primary disinfectant during a project managed by the Ohio River Valley Water Sanitation Commission.[18] For this investigation, the routine practice was source water chlorination, potassium permanganate treatment, coagulation, settling, GAC filtration/adsorption, and free chlorine application in the clearwell. Later, the treatment train was modified to inject chlorine dioxide and potassium permanganate into the source water entering the coagulation basin, with free chlorine used as a secondary disinfectant in the clearwell before distribution. Chlorine dioxide dosage to the source water was 1.5 mg/L and contained less than 0.1 mg/L of chlorine.

Bacteriologic data presented in Table 81 (page 217) indicate that 1.5 mg/L of chlorine dioxide was less effective as a source water disinfectant than was 2.6 mg/L chlorine. During source water chlorination, mean total coliform and standard plate count densities in the activated carbon/filter adsorber influent were 1/100 mL and 50/mL, respectively. When chlorine dioxide was the applied disinfectant before coagulation and settling, a disinfectant residual could not be maintained. As a result, mean bacterial densities reaching the activated carbon filter/adsorber were 43 total coliforms/100 mL and 7,100 standard plate count organisms/mL. In-plant survivors of the total coliform population passed through the 2-1/2-year-old Filtrasorb® 400 GAC filter/adsorber essentially unchanged in density. In both treatment trains, the secondary application of chlorine in the clearwell was, however, an effective barrier to detectable coliform penetration into the distribution system.

These data indicate that 1.5 mg/L of chlorine dioxide evidently was not equal to the disinfection effectiveness of free chlorine during source water disinfection. Increasing the dose of chlorine dioxide was not economically feasible and might exceed the limit of 0.5 mg/L residual chlorine dioxide, chlorite, and chlorate recommended by the USEPA.[3]

In the next modification evaluated at this water plant, the chlorine dioxide feed to the source water was lowered to 1.0 mg/L, and source water chlorination (1.2 mg/L) was also practiced. Source water ammonia concentrations during this period were unusually high, averaging 0.6 mg/L.

Bacteriologic data presented in Table 82 (page 218) indicate that source water disinfection with a lower concentration of both disinfectants was effective in reducing the bacterial densities in the GAC filter/adsorber influent, but some regrowth of total coliforms and the standard plate count organisms did occur in the filter/adsorber and appeared in the effluent. With the application of chlorine at the clearwell, however, the finished water did meet the bacteriologic standard for total coliforms, and a low mean standard plate count of 8 organisms/mL was present.

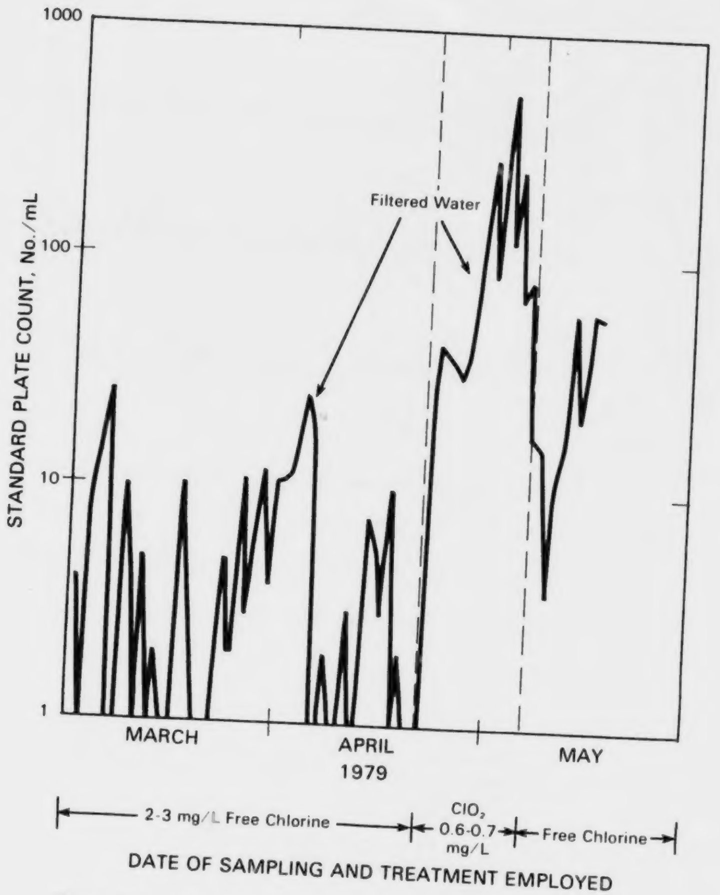

Figure 115. Standard plate counts for periods of disinfection with free chlorine and chlorine dioxide at the Louisville Water Company (KY).[178] (Adapted from JOURNAL American Water Works Association, Volume 73, No. 2 [February 1981] by permission. Copyright 1981, the American Water Works Association.)

At Evansville, IN, a Micro-Floc Water Boy®* pilot water treatment unit was used to study chlorine dioxide as an alternative to chlorination as routinely applied by the treatment plant.[63] Basically, the pilot plant treatment consisted of disinfection and alum and polymer addition to the source water. This chemically treated water was mixed, flocculated, and then clarified in a tube settler. Clarified water then passed through a mixed-media filter and onto two GAC post-filter adsorbers before reaching a clearwell. In an effort to simulate a dead-end in a distribution system, an iron pipe 10 cm (4 in) in diameter and 11 m (36 ft) long was connected to the end of the pilot plant.

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*Manufactured by Neptune Micro Floc, Corvallis, OR 97330

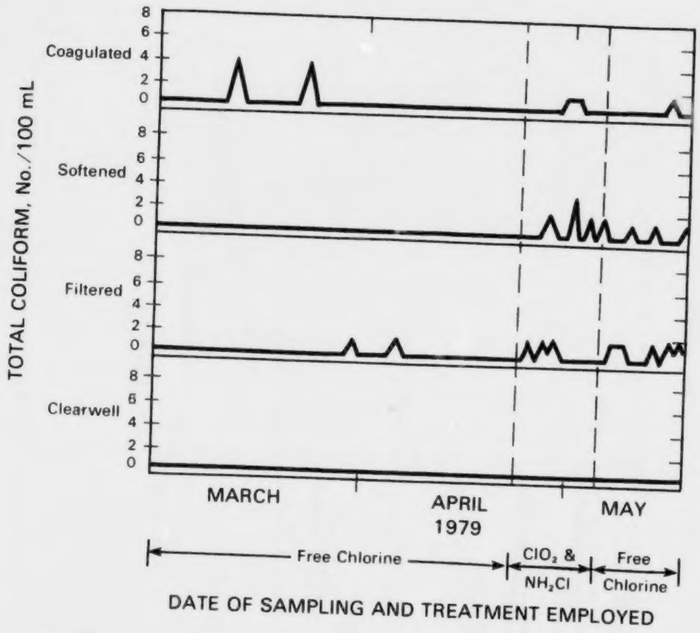

Figure 116. Total coliform density for in-plant processes during periods of free chlorine and chlorine dioxide disinfection at the Louisville Water Company (KY).[178] (Adapted from JOURNAL American Water Works Association, Volume 73, No. 2 [February 1981] by permission. Copyright 1981, the American Water Works Association.)

The full-scale water treatment plant at Evansville, IN, involves source water chlorination (6.6 mg/L), coagulation and settling, pH adjustment, and rapid sand filtration. Booster chlorination is used ahead of the clearwell only during periods when the chlorine residual falls below 1.0 mg/L as the water enters the distribution system. Because of the similarity of preliminary data obtained from both the full-scale treatment and pilot plants during parallel studies with identical chlorination applications, the full-scale treatment plant was viewed as a suitable control for disinfection effectiveness.

A study of data collected from three runs over an 11-month period revealed that chlorine dioxide treatment of the source water was effective in reducing the total coliform and standard plate count populations, but not always to the level observed with chlorination of the same water in the full-scale operation (Table 83, page 219). Because chlorine dioxide was not present in the GAC post-filter adsorber effluent, a booster application of chlorine dioxide was applied to the clearwell influent. This secondary disinfectant application to achieve a chlorine dioxide residual was effective in producing a finished water of essentially the same high quality as obtained in the full-scale plant operation.

Regrowth of standard plate count organisms occurred in the GAC adsorbers during warm-water conditions and was more pronounced in virgin activated carbon (Adsorber #1) than in reactivated carbon (Adsorber #2). Although the total coliform count did not increase in the reactivated carbon adsorbers during the warm period,

TABLE 81. CHLORINE DIOXIDE APPLICATION STUDY USING MONONGAHELA RIVER SOURCE WATER AT THE WESTERN PENNSYLVANIA WATER COMPANY[18]

	Sample point (mean values*)											
	Cl_2 application to source water†						ClO_2 application to source water‡					
Parameter	Source water	Plant influent	Coagulated water	Settled water	GAC-filtered water	Finished water	Source water	Plant influent	Coagulated water	Settled water	GAC-filtered water	Finished water
Flow time, hr	0	0.5	3.75	12.5	13.5	14.75	0	0.5	3.75	12.5	13.5	14.7
Turbidity, ntu	51	38	5.7	8.5	0.6	0.2	6.8	5.2	6.3	2.3	0.3	0.2
Total coliforms/ 100 mL	21,000	4	1	1	8	<1	14,000	4,200	100	43	44	<1
Standard plate count/mL	§	490	200	50	150	3	§	29,000	4,790	7,100	850	1
pH	7.2	7.1	7.3	7.1	7.2	7.1	7.1	7.1	7.5	7.4	6.9	6.8
Free Cl_2 residual, mg/L	§	0.4	<0.1	<0.1	<0.2	0.6	§	**	<0.1	<0.1	0.1	<0.4
ClO_2 residual, mg/L	§	§	§	§	§	§	§	**	<0.1	<0.1	<0.1	<0.1
Total Cl_2 residual, mg/L	§	0.8	0.4	0.3	0.2	0.8	§	§	§	§	§	§
		↑ Chlorine, 2.6 mg/L				↑ Chlorine, 1.1 mg/L			↑ Chlorine dioxide, 1.5 mg/L			↑ Chlorine, 1.4 mg/L

*Cl_2 study based on five samples over a 10-day period; ClO_2 study based on four samples over a 6-day period.
†Source water temperature, 22°C (72°F).
‡Source water temperature, 27°C (81°F).
§Not run.
**Not detected.

TABLE 82. STUDY OF CHLORINE DIOXIDE APPLICATION TO SOURCE WATER WITH BACKGROUND AMMONIA USING MONONGAHELA RIVER SOURCE WATER AT THE WESTERN PENNSYLVANIA WATER COMPANY[18]

Parameter	Sample point (mean values*)					
	Source water	Plant influent	Coagulated water	Settled water	GAC-filtered water	Finished water
Flow time, hr	0	0.5	3.75	12.5	13.5	14.75
Turbidity, ntu	12	7.9	6.2	2.7	0.1	0.1
Total coliforms/ 100 mL	14,000	2,000	<1	<1	2	<1
Standard plate count/ mL	†	5,900	66	33	440	8
pH	7.1	7.1	7.2	7.7	7.0	6.9
Free Cl_2 residual, mg/L	§	<0.1	‡	<0.1	‡	0.1
ClO_2 residual, mg/L	†	‡	<0.1	‡	‡	<0.1
Total Cl_2 residual, mg/L	†	0.8	1.1	0.9	<0.1	0.7
		↑ Cl_2 application, 1.2 mg/L	↑ ClO_2 application, 1.0 mg/L			↑ Cl_2 application, 1.1 mg/L

*Based on 4 samples over 4-day period; source water temperature, 25°C (77°F).
†Not run.
‡Not detected.

they did persist at low levels. Loss of a chlorine dioxide residual through the latter stages of treatment also contributed to further bacterial penetration in the treatment train during this warm-water period.

Instantaneous Disinfection—

Maintaining a free chlorine residual for only a short time period is an effective method of reducing the formation of trihalomethanes (see Section VIII). To achieve adequate disinfection during such a short contact period requires high-intensity, instantaneous mixing of chlorine with every portion of the water being treated. A research project is under way to test the applicability of this approach at the University of Texas at San Antonio.[138] In this investigation, disinfectant is introduced by means of high energy in-line mixing (G = about 40,000 sec^{-1}) to a 410-m^3/day (75-gpm) flow stream. After 16 seconds of contact time, the water passes through a second high energy (G = about 40,000 sec^{-1}) in-line mixer. Flow continues in a pipe loop for 55 seconds to provide short but precisely known contact times. Longer contact times for disinfection or trihalomethane formation are obtained by collecting samples of water discharged from the pipe loop and holding them for the desired time period.

In these experiments, coliform bacteria were fed into the undisinfected, filtered water as it was pumped from a holding tank into the disinfection system. The total coliform data (Table 84) indicate that effective disinfection could be achieved without producing high concentrations of trihalomethanes when the rapid, high-energy, plug-flow mixing system was used. Addition of ammonia after 16 seconds eliminated the free chlorine residual, thereby limiting the trihalomethane formation (see Table 52 in Section VIII). Because of the very efficient mixing attained in this system, most of the coliform inactivation occurred within 15 seconds

TABLE 83. PILOT PLANT EVALUATION OF CHLORINE DIOXIDE USED AS AN ALTERNATIVE DISINFECTANT[83]

Treatment stage	Test run No. 1*		Test run No. 2†		Test run No. 3‡	
	SPC**/ mL	Total coliforms/ 100 mL	SPC/ mL	Total coliforms/ 100 mL	SPC/ mL	Total coliforms/ 100 mL
Pilot plant (ClO_2 applied to source water):						
Ohio River intake	8,000	32,000	6,300	18,000	1,700	2,900
Settled water	92	<1.0	110	<1.0	94	<1.0
Mixed media effluent (GAC influent)	77	1.0	76	1.9	1.4	<1.0
GAC No. 1, effluent	760	<1.0	6,200	1.6	16	<1.0
GAC No. 2, effluent	390	1.3	330	<1.0	12	<1.0
Clearwell	2.6	<1.0	7.9	<1.0	1.6	<1.0
Simulated dead end	19,000	<1.0	7,100	<1.0	5,300	<1.0
Full-scale plant (source water chlorination):						
Ohio River intake	8,800	32,000	6,300	18,000	1,700	2,900
Settled effluent	13	<1.0	10.9	<1.0	6.2	<1.0
Clearwell influent	<1.0	<1.0	1.6	<1.0	1.0	<1.0

*April 23 to July 27, 1979; total samples per site = 65; source water temperature, 22°C (72°F).
†Sept. 17 to Dec. 11, 1979; total samples per site = 52; source water temperature, 16°C (61°F).
‡March 4 to June 3, 1980; total samples per site = 62; source water temperature, 14°C (57°F).
**Standard plate count.

TABLE 84. EFFECTIVENESS OF DISINFECTION IN A HIGH-INTENSITY MIXING SYSTEM[138]

Disinfection system		Total coliforms					
		Control		Surviving organisms/100 mL			
Dose, mg/L	Agent(s)	pH	No./100 mL*	15 sec	56 sec	15 min	60 min
0.5	Chlorine	†	8,900,000	<30	<30	<30	<30
0.5	Chlorine + ammonia‡	7.7	170,000	<30	†	<30	<30
0.5	Ammonia + chlorine‡	†	11,000,000	87,000	15,000	<30	<30
0.5	Chlorine dioxide	†	12,000,000	<30	<30	<30	<30
1.5	Chlorine	7.7	15,000,000	<30	<30	<30	<30
1.5	Chlorine + ammonia‡	7.6	280,000	†	<30	†	†
1.5	Ammonia + chlorine‡	†	8,200,000	7,000,000	<30	<30	<30
5.0	Chlorine	7.5	11,000,000	<30	<30	†	†
5.0	Chlorine + ammonia‡	7.9	5,800,000	<30	<30	<30	<30
5.0	Ammonia + chlorine‡	†	6,000,000	50,000	<30	<30	<30

*Standard plate count.
†Not run.
‡Ammonia dose in mg/L equal to chlorine dose in mg/L.

and before ammonia was added. Disinfecting action during this brief time period was less effective, however, when ammonia was added first and followed by chlorine 15 seconds later.

High-intensity, rapid disinfectant mixing was less effective for inactivating the standard plate count organisms to the same order of magnitude. This weaker response to controlling a wide spectrum of organisms may affect the selective nature of surviving organisms released into the distribution system, their ability to become established in the distribution network, and the need for longer contact times or higher concentrations of chloramines in treatment and distribution. Further investigations of this treatment concept should be made in field studies of water systems in different geographical areas.

An unpublished study by the North Jersey Water Supply Commission did present one field opportunity to study the concept of short-term mixing of free chlorine. This water supply district maintains twin, cement-lined steel mains, 1.9 m (74 in) in diameter, from the Wanaque Reservoir to the Little Falls treatment plant. Following chlorination, lime is added for pH adjustment, and the water is then transmitted to the consumer. A filtration plant is being built but is not yet operational. The use of twin transmission lines created the opportunity to add ammonia to one of the lines. The time between injection of chlorine and sufficient ammonia to convert free chlorine to chloramines was estimated at less than 1 minute. The flow in each line was great enough to provide intense mixing.

As a measure of disinfectant efficiency, standard plate counts were determined after 1 minute of contact time and following the 6-hour flow in both transmission lines. Inspection of the winter data (1-4°C [34-39°F]) revealed no significant difference in residual bacterial densities after exposure to short-term mixing with free chlorine and after 6 hours of contact time with or without ammoniation (Table 85). Apparently, maximum disinfection effectiveness was provided instantaneously because of the intense mixing; no significant further reductions were achieved by extending contact time with either type of disinfectant residual. Coliforms/100 mL were detected neither in water leaving the high-intensity mixing location nor in the transmission lines after 6 hours of contact time. During the following summer, both types of high-intensity disinfection were again studied bacteriologically, and the data indicated an even more effective reduction (10-fold) in the standard plate count. Again, no coliforms/100 mL were detected after 1-minute contact or following 6 hours flow in both transmission lines. Finally, the addition of ammonia prevented the formation of trihalomethanes (see Section VIII, Subsection, Formation of Trihalomethanes).

Impact on Distributed Water Quality

The data presented in the previous subsection relate to the bacteriologic quality of finished water. Modifications in treatment train processes to reduce trihalomethane production may ultimately change the character of the bacterial populations passing through the distribution system. These quality changes may be of immediate concern if the last barrier to bacterial passage into the finished water is interrupted, if changes occur seasonally with increased water temperature or slowly with time as habitats develop and the microflora adjust to changes in this water environment.

In the Louisville Water Company study of chlorine dioxide as an alternative disinfectant, bacteriologic data from the distribution system were reviewed for any significant changes.[178] Data points in Figure 117 represent the average values for 8 to 12 daily distribution system samples collected over 29 days before the use of chlorine dioxide treatment, 10 days during the treatment modification, and for 5 days after routine chlorination was restored. Standard plate count densities averaged approximately 83, 87, and 65 organisms/mL before, during, and after disinfection with chlorine dioxide, respectively, suggesting that a slight lowering of the bacterial population occurred during treatment modification. Because the treatment

TABLE 85. FIELD STUDY OF HIGH-INTENSITY MIXING OF CHLORINE*

Date 1979	Temperature		Standard plate count, No./mL			
			Chlorination station,† contact time, <1 min		Little Falls plant,† contact time, 6 hr	
	°C	°F	Combined Cl_2§	Free Cl_2‡	Combined Cl_2§ **	Free Cl_2‡#††
Jan 10	4	39	23	24	26	16
Jan 19	2	36	26	11	#	#
Jan 26	2	36	28	32	23	16
Jan 30	2	36	65	45	38	43
Feb 6	2	36	54	49	41	47
Feb 14	1	34	38	35	25	27
Feb 20	1	34	#	#	28	31
Feb 26	1	34	#	#	27	22

*Source: Unpublished data from North Jersey District Water Supply Commission.
†pH range, 8.5 to 9.1.
‡Cl dose = 2.2 to 2.4 mg/L.
§Cl dose = 1.2 to 2.4 mg/L; NH_3 dose = 0.3 to 0.65 mg/L.
**Free residual Cl_2 = <0.1 mg/l; total residual Cl_2 = 0.9 to 1.2 mg/L.
††Free residual Cl_2 = 0.6 to 1.0 mg/L; total residual Cl_2 = 0.8 to 1.0 mg/L.
#Not run.

modification period was only 17 days, no long-term effects on distribution water quality could be determined, but the initial results were encouraging.

The Cincinnati Water Works stopped chlorination of the Ohio River source water and began chlorinating at the influent to the treatment plant on July 14, 1975, as an initial step in changing the in-plant water treatment process to control trihalomethanes (see Section VII, Subsection Cincinnati, OH, Results). Chlorination at the clearwell was used to inactivate any residual coliform population that might have penetrated other processes in the treatment chain. With careful control of chlorine dose, point of application, and water pH, a significant decrease in trihalomethane concentration was realized (see Figure 63 in Section VII). The impact that this treatment modification might have on the bacteriologic quality of drinking water at the distribution system dead-ends and other slow-flow sections in the distribution network was determined from an intensive 2-year study.[179]

With the cooperation of the Cincinnati Water Works Water Distribution Maintenance Section, samples from 32 dead-end water mains were examined on a rotating basis of eight sites per week. These sites are among a number of troublesome dead-end water mains that are flushed out each week to clear accumulated sediments and bring fresher waters with free chlorine residuals into these distribution lines. Samples from these flushes were iced immediately and processed within 5 hours of collection. Analyses of 613 water samples over the 2-year period included a 10-tube, three-dilution total coliform most probable number (MPN) and a standard plate count incubated at 35°C (95°F) for 48 hours. Physical/chemical parameters measured were free chlorine residual, turbidity, water temperature, and pH. Results for an 18-month portion of the study that included 8 months of data before the treatment modification are given in Figure 118.

Changes in water quality in the distribution system were not observed immediately on the day of the treatment change. Approximately 15 days passed before some decrease in free chlorine residual concentrations, turbidity, and pH occurred. Before the change in the point of disinfection application, increased chlorine residuals were inconsistent in limiting some coliform occurrences, probably because of sediment accumulations that resulted in an average turbidity of 20.7 ntu in these dead-end sections (see Figure 118). The most extreme example occurred during one week in December 1974, when the total coliform density averaged 138 organisms/100 mL in the eight samples collected from selected dead-end flushings. Once the turbidity

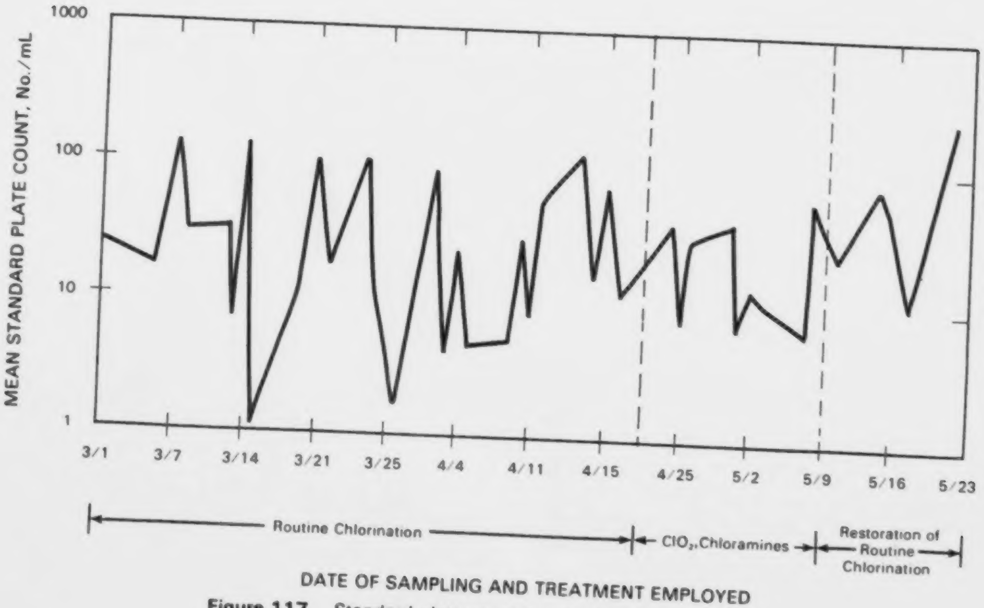

Figure 117. Standard plate count for distributed water before, during, and after disinfection with chlorine dioxide at the Louisville Water Company (KY). Data points represent averages of 8 to 12 daily distribution system samples.[178] (Adapted from JOURNAL American Water Works Association, Volume 73, No. 2 [February 1981] by permission. Copyright 1981, the American Water Works Association.

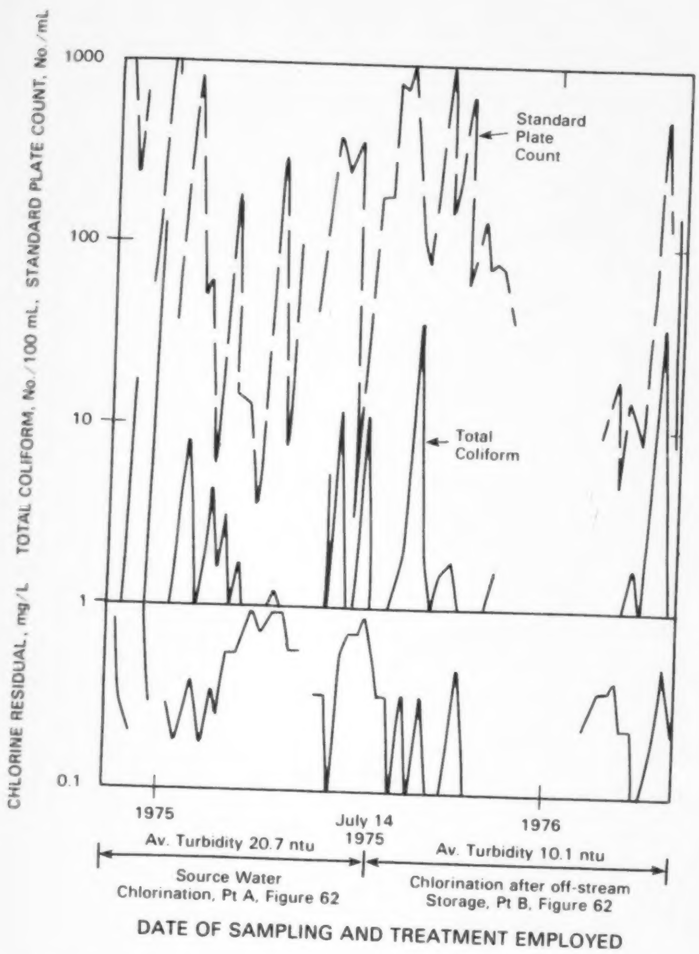

Figure 118. Bacteriologic quality of water in dead ends of the Cincinnati, Ohio, distribution system after changes in point of chlorine application.

decreased to an average of 10.1 ntu, this interference with disinfection was not apparent. Why the turbidity in the dead-ends was reduced following the treatment change is not known; the protocol and frequency of main flushing remained unchanged. Perhaps this reduction in turbidity was a result of more water flow with increased tap-ins from residential developments or it may have been a result of more stable scale formation on the pipe walls (pH shifted from 8.0 to 7.8) following treatment modifications.

After the point of chlorination was moved, a free chlorine residual concentration of at least 0.2 mg/L was effective in controlling coliform occurrences in the dead-end sections of the distribution network (Figure 118). When free chlorine residual concentrations declined to 0.1 mg/L or less, however, coliforms in protected pipe habitats reached the sampling sites in a viable state and were detected in densities as great as 10 organisms/100 mL. During warm-water periods, when free chlorine residual concentrations occasionally declined to 0.1 mg/L or less, some coliform regrowth occurred, with densities ranging from 12 to 30 organisms/100 mL. Water temperatures during these periods of low free chlorine residual concentrations ranged from 20 to 25°C (68 to 77°F). Finally, sudden increases in standard plate count densities often occurred a few days to a week in advance of the appearance of coliforms in these waters. Standard plate counts would thus serve as an early signal of undesirable quality changes occurring in water distribution systems or during a loss of disinfection effectiveness.

Disinfectant Stability during Water Distribution

Stability of disinfectants during water supply distribution is important for a number of purposes, particularly to prevent colonization of surviving organisms and protection from the intrusion of contamination in the pipe network. Microbial colonization may lead to corrosive effects on the distribution system and aesthetic effects such as taste, odor, and appearance. Regrowth of potential health-related opportunistic organisms and their impact on coliform detection should not be dismissed as a trivial problem. Further, the maintenance of a biocidal residual to the consumer's tap keeps the system clean and protects against some cross-connection contamination, and its sudden disappearance is a rapid indication of distribution system problems. While maintenance of a disinfectant residual in the distribution system will not stop massive levels of external gross contamination that are detectable through odors, color, and milky turbidities, it may quickly inactivate pathogens in the more frequent cases associated with contaminants seeping into large volumes of high-quality potable water.[180]

Distribution system problems associated with the use of combined chlorine residual or no residual have been documented in several instances.[181-183] In these cases, the use of combined chlorine is characterized by an initial satisfactory phase in which chloramine residuals are easily maintained throughout the system and bacterial counts are very low. Over a period of years, however, problems may develop, including increased bacterial counts, dropoff of chloramine residuals, increased taste and odor complaints, and reduced main carrying capacity. Therefore, as noted later, increased monitoring is recommended if this technique of trihalomethane control is practiced.

Discussion

Drinking water treatment modifications to reduce trihalomethane precursors and thus control trihalomethane concentrations must be cautiously applied. Careful consideration must be given to the changes such alterations may introduce in the bacteriologic quality of drinking water produced in the plant and transmitted through the distribution network. Not all source waters are of uniform bacteriologic quality; thus adequate treatment barriers must be maintained at all times to meet changing water qualities. In all field studies reported in this volume, no overt evidence was found to indicate the bacteriologic deterioration in the finished water leaving the treatment plant. In the trade-off to decrease trihalomethane concentrations by delaying disinfection, however, some critical reductions of bacterial population later in the treatment train must be accepted. Greater reliance must therefore be placed on effective, continuous final disinfection, with maintenance of a disinfectant residual in the distribution system to counter effectively the residual coliform populations and associated pathogens that have survived earlier stages of water treatment.

Monitoring during Heavy Pollution Loads—

Bacterial penetration of the multiple barriers in the drinking water treatment process is more pronounced during abnormal pollution loads in the source water. Under these circumstances, expected bacterial decreases during the early phases of the treatment chain will not adequately suppress the residual bacterial population. This condition places a greater burden on the last in-plant treatment barrier—disinfection. A daily bacteriologic monitoring of all in-plant processes is therefore recommended during periods of abnormal increases in source water pollution (determined from baseline monitoring data) to evaluate the transport and fate of the total coliform and general bacterial population through the treatment chain.

Monitoring Systems with GAC Adsorbers—

Treatment systems incorporating GAC adsorbers present some unique bacteriologic monitoring problems. Substantial bacterial growth in GAC adsorbers can occur, the flora being a reflection of source water organisms (including coliforms) that survive early treatment processes. Changes in organism dominance occur partly because of habitat site selection, competition with other members of the bacterial flora, and available nutrients adsorbed onto activated carbon particles.

Ozonation—Ozonation of influent waters before they pass through activated GAC adsorbers has three effects: 1) It provides more nutrients for microorganisms by making some organic compounds more biodegradable; 2) it restricts the number and kinds of organisms reaching the adsorber bed, and 3) it accelerates the growth of survivors by inactivating bacterial antagonists and competitors for available nutrients. The net result can be the release of substantial numbers of bacteria (many of which may be selectively resistant to disinfection) into the GAC adsorber effluent.

GAC Adsorption without Prior Disinfection—In water plant modifications involving GAC adsorption without prior disinfection, coliform survivors may become established in the GAC bed under warm ambient temperatures and ultimately migrate into the adsorber effluent. Because of the potential problem of coliform regrowth and release of a highly specialized bacterial population from the GAC adsorber, bacteriologic monitoring of the adsorber effluent is recommended as part of in-plant quality assurance, especially during periods when water temperatures rise above 12°C (54°F). Such monitoring data would serve as an early warning of bacterial penetration of the treatment train. The operator could then evaluate the need for backwashing the adsorbers to reduce bacterial buildup and the need for increasing the dose of disinfectant in the final treatment process.

Concepts for Measuring Bacterial Populations—If bacterial densities in GAC adsorbers are to be adequately characterized, traditional concepts for measuring the general bacterial population must be revised. These organisms are not easily cultivated, either on standard plate count agar or at 35°C (95°F). Thus consideration should be given to optimizing their detection by using 28°C (82°F) incubation for 7 days. Furthermore, a medium such as R-2A agar or soil extract agar is desirable for recovery of a broad spectrum of this specialized population.

Bacteriological Quality of Finished and Distributed Water—

Although field studies have demonstrated that the treatment modifications recommended in this volume will not adversely affect the bacteriologic quality of finished water, they will result in a lowered bacterial barrier, particularly during warm-water periods or during the occurrence of gross deteriorations in the bacteriologic quality of source waters. For this reason, final application of a disinfectant and establishment of a disinfectant residual become the critical treatment barriers that must be maintained continuously in a high state of effectiveness. Continuous monitoring for a disinfectant residual is recommended for these modified treatment systems, and these measurements should be supported by daily turbidity and bacteriologic measurements to assure proof of disinfection effectiveness.

In systems using GAC adsorbers, the bacteriologic quality of finished water during warm-water periods should be determined (every 4 to 6 hours) whenever a sudden turbidity change occurs in the GAC adsorber effluent to ensure that high densities of bacteria in GAC adsorber effluents do not penetrate the disinfection barrier. Ideally, an automated, programmable sampling device that includes provision to perform the rapid (7-hr) fecal coliform measurement or an ATP measurement would be desirable to maintain a closer vigil for early evidence of bacterial penetration of the treatment barrier.

Long-term bacteriologic effects of treatment modifications will most likely be observed first in the slow-flow and dead-end sections of the distribution network. These locations are also the sites where new waterborne organisms passing through treatment frequently establish their initial habitats in the accumulated sediments. When treatment modifications are proposed, gathering baseline data at these locations over a 6-month period and continuing this monitoring for at least 1 year following in-plant modifications would be desirable. In monitoring in-plant treatment changes for trihalomethane control, slow-flow and dead-end sections in the distribution system should be monitored weekly during warm-weather periods (when temperatures are above 12°C [54°F]) for both total coliforms and standard plate count. Sampling of dead-end sections should be done on a weekly basis, rotating site locations to include all major dead ends in the network during the warm season. Reliance on sample collections made from the main flow in the distribution system is misleading because of high disinfectant residuals. These samples may give no immediate indication of subtle changes beginning to occur at more remote sites in the network that relate to ineffective disinfectant residuals and intermittent penetration of the treatment barrier.

SECTION X
TREATMENT COSTS

Background

Treatment costs are concerned with analyzing the unit process costs associated with the various technologies that could be most efficiently used to meet the trihalomethane MCL[3] using each of three possible approaches. Not every unit process is equally efficient in accomplishing the goals of meeting the MCL: Some are much more efficient in removing trihalomethanes after formation, some remove trihalomethane precursors most efficiently, and several alternative disinfectants other than free chlorine are available.

This section is designed to assist the utility manager, the consultant, the Primacy Agency, and others in achieving economical, feasible strategies for meeting the THM Regulation.[3] To combine process efficacy and cost in selecting appropriate unit processes, use this section along with others in this book; the presentation is such that processes can be selected on comparative costs for equivalent performance basis.

An attempt has been made to identify variables such as reactivation frequency and chemical dose, and the sensitivity of alternative strategies to these design criteria variables has been taken into account. The figures presented herein can be used in conjunction with pilot testing to evaluate costs for a wide range of alternatives. Although the costs are based on 37,800 m^3/day and 378,000 m^3/day (10 and 100 mgd) for the most part, Figure 119 can be used to estimate economies of scale that might result from size differentials. Twenty years, rather than the normal 30 to 40 years, was selected as the amortization period for the unit processes considered. This was done to be conservative and to reflect the use of new or relatively untried technology and to provide a reasonable basis for comparison among processes. Cost calculations in Section XI will compare performance and cost considerations.

The unit costs are based on point estimates and should be considered as preliminary or planning estimates only. For more complete and detailed cost analysis, including sensitivity analysis, see the references cited in Section XII. Additional data are being collected concerning the cost and performance of the unit processes discussed in this section. Realistically, cost data developed in this analysis should be considered accurate in a relative sense. In a site-specific situation, particular circumstances may influence the amount or cost of an input factor (labor hours or $/labor hour, for example) required to produce a given water quality output.

This section deals with costs for the technology most closely associated with each of the three control approaches discussed previously. Treatment techniques discussed for the first approach (removal of trihalomethanes) are diffused-air and tower-aeration and special adsorption resins. Methods discussed for the second approach (removal of trihalomethane precursors) include clarification, coagulation-sedimentation-filtration, direct filtration and precipitative softening, PAC and GAC adsorption, ion exchange resins, the combination of ozone and ultra-violet radiation (O_3/UV), and the combination of ozone and GAC adsorption. Discussion of the third approach (alternative disinfectants) involves cost comparisons of chlorination, ozonation, chlorine-ammonia, and chlorine dioxide treatment. Many of the cost data used in this section were derived from a study prepared for USEPA by Culp/Wesner/Culp Consulting Engineers.[184]

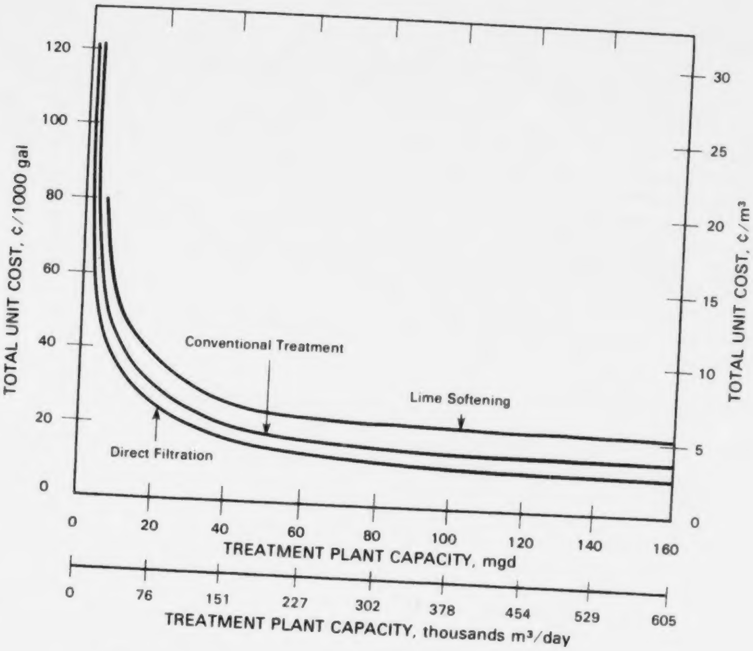

Figure 119. Total treatment unit costs vs. plant capacity.

General Considerations

For each unit process and combination thereof, the assumptions made for the cost analysis will be given, followed by a graphic presentation of the influence of key variables on the total treatment cost—i.e., amortized capital costs plus operation and maintenance (O&M) costs.[185] Finally, specific cost figures for one given set of assumptions will be presented.

The choice of a set of assumptions is not intended to reflect performance levels between processes but only to reflect costs within typical design levels. Pilot studies should be done to provide comparative performance information. Table 86 contains the cost assumptions used in each of the calculations.

TABLE 86. COST ASSUMPTIONS USED THROUGHOUT SECTION X

Item	Level
Energy	$0.04/kWh
Labor	$10.00/hr
Producers Price Index (1980)	243.8
Engineering News Record Index (1980)	325.0
Interest rate	8 percent
Amortization rate	20 yr

Economies of Scale

One of the general issues that relates to cost estimating for water supply technology is that of economies of scale. As the size of the facility decreases the unit cost of the facility tends to increase. Figure 119, the unit costs for conventional treatment, direct filtration, and precipitative softening illustrate this effect. This figure is based on a specific set of assumptions that will be discussed more completely in the Subsection Removal of Trihalomethane Precursors, below. The "scale effect" is, however, one that will apply to all technologies over the size ranges discussed. For example, in Figure 119, the cost of conventional treatment at 37,800 m^3/day (10 mgd) is approximately 8¢/m^3 (30¢/1000 gal); at 18,900 m^3/day (5 mgd), 10¢/m^3 (36¢/1000 gal); and at 3,780 m^3/day (1 mgd), 11¢/m^3 (42¢/1000 gal). These same percentage changes in cost with facility size can be applied to all of the technologies discussed in the following section as an approximate technique for estimating scale economies.

Cost Analysis Results

Removal of Trihalomethanes—

Diffused-Air Aeration—Diffused-air aeration involves passing air through the process flow stream. For this analysis, this is assumed to take place in open, reinforced concrete basins with direct-drive centrifugal compressors and porous diffusors placed at close intervals over the entire basin flow for air introduction. Process energy requirements include the operation of the air compressors 365 days/year, 24 hours/day. Maintenance materials include lubricants and replacement components for air compressors and air diffusion equipment. Estimates were developed from a review of costs associated with activated sludge aeration facilities. Labor requirements include maintenance of air compressors, air piping, valving and diffusors, and aeration basins. Table 87 contains some of the key assumptions used in calculating the costs associated with diffused-air aeration.

The effectiveness of using aeration as a technique for stripping trihalomethanes depends heavily on the air/water ratios used (see Section VI, Subsection Diffused-Air Aeration). In turn, the cost of diffused-air aeration also depends on the air/water ratio. With the use of the design assumptions in Table 87, total treatment costs were calculated (Figure 120) for diffused-air aeration systems with air/water ratios ranging from 1:1 to 30:1, and capacities of 37,800 and 378,000 m^3/day (10 and 100 mgd).* The systems were assumed to be operating at 70-percent capacity. A breakdown of costs (O&M, capital, and total) for the same systems operating at 70-percent capacity with a 20:1 air/water ratio is shown in Table 88.

TABLE 87. DIFFUSED-AIR AERATION ASSUMPTIONS

Item	Assumption
Basin depth	3.3 m (10 ft)
Air supply	1.52 sm^3/m^2 (5 scf/ft^2)

Aeration Towers—Stripping of trihalomethanes from water can be accomplished in aeration towers similar to those used for oxidation of iron and manganese (see Section VI, Subsection Tower Aeration). As with diffused-air aeration, the degree of removal of a specific organic compound by this technique depends on the Henry's

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* These capacities are used throughout this section to reflect the differences between small and large treatment plants. A 37,800-m^3/day (10-mgd) treatment plant operating at 70-percent capacity would serve a population of 75,000 the size covered by the first phase of the Trihalomethane Regulation.[1] Costs for smaller treatment plants are currently being collected and will be available before November 29, 1983, when the second phase of the Trihalomethane Regulation[1] becomes mandatory.

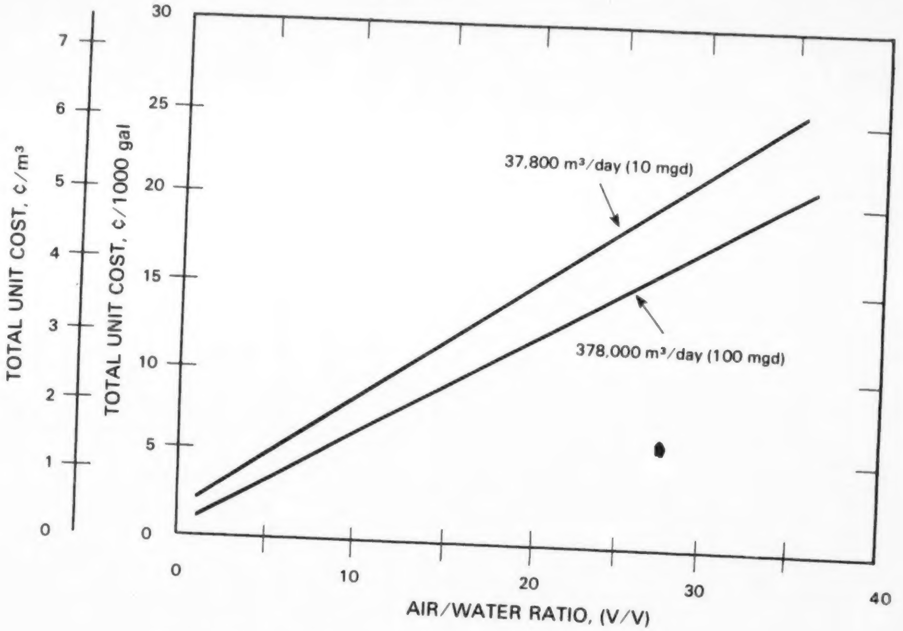

Figure 120. Total treatment unit costs for diffused-air aeration systems, 37,800- and 378,000-m³/day (10- and 100-mgd) capacities.

TABLE 88. CAPITAL AND O&M COSTS FOR A DIFFUSED-AIR AERATION SYSTEM OPERATING AT 70-PERCENT CAPACITY WITH A 20:1 AIR/WATER RATIO

	System treatment capacity			
	37,800 m³/day (10 mgd)		378,000 m³/day (100 mgd)	
Item	¢/m³	¢/1000 gal	¢/m³	¢/1000 gal
O&M cost	2.0	8.2	1.1	4.5
Capital cost	1.8	7.1	1.8	7.3
Total treatment cost	3.8	15.3	2.9	11.8

law constant of the compound, the air/water ratio, water temperature, and many other factors.

Estimated construction costs are for rectangular aeration towers with polyvinyl chloride (PVC) packing media. For towers smaller than 178 m^3 (6,400 ft^3), units are shipped assembled and have fiber-glass skins supported by a galvanized metal framework. Towers of greater volume are field-erected from factory-formed components and are similar in design and construction to industrial cooling towers. The exterior skin of corrugated asbestos-cement panels is attached to a structural steel framework. Towers are supported on reinforced concrete basins. The basin collects tank underflow and serves as a sump for the pump.

The cost estimate presented here includes the tower supply pumps and tower underflow pumps. These aeration towers have electrically driven, induced-draft fans with fan stacks and drift eliminators. Process electrical energy requirements are for operation of the induced-draft fan, assuming a 24-hour/day, 365-day/year operation. In some instances where pumping energy may also be required, it is estimated separately as part of the unit operation cost; but pumping head will vary from application to application. Units are assumed *not* to be housed, eliminating the need for building-related energy. Some localities may have to consider protecting the unit(s) from inclement weather, which would incur an additional cost. Table 89 contains the assumptions used in calculating tower aeration costs.

TABLE 89. AERATION TOWER ASSUMPTIONS

Item	Assumption
Tower height	6.1 m (20 ft)
Pumping	9.1 m (30 ft) total dynamic head
Air supply	15.92 sm^3/m^2 (52.25 scf/ft^2) of tower surface area

As with diffused-air aeration, the effectiveness of tower aeration depends heavily on the assumed air/water ratio. Total treatment costs are calculated for tower aeration systems with air/water ratios ranging from 1:1 to 800:1 (Figure 121). A breakdown of costs (O&M, capital, and total) for these systems operating at an average 70-percent capacity for an air/water ratio of 500:1 is given in Table 90. Some tradeoffs are possible—for example, increasing the tower depth versus increasing the air/water ratio to achieve increased removal of volatile organics. These options are explored as follows.

Based on the assumptions used in this analysis, several mechanisms are available for removing volatile organics. One option for a given tower depth would be to increase the surface area of the tower, thereby increasing the amount of air induced into the water stream. Another option would be to fix the surface area of the tower

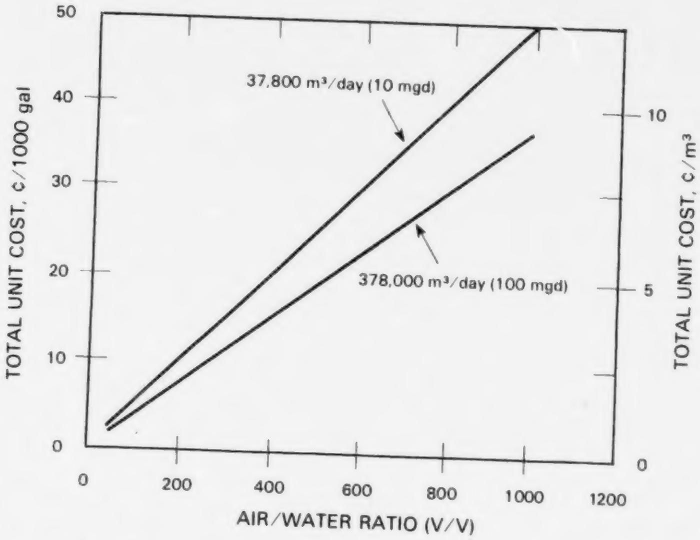

Figure 121. Total treatment costs for tower aeration systems, 37,800- and 378,000-m^3/day (10- and 100-mgd) capacities.

TABLE 90. CAPITAL AND O&M COSTS FOR A TOWER AERATION SYSTEM OPERATING AT 70-PERCENT CAPACITY WITH A 500:1 AIR/WATER RATIO

	System treatment capacity			
	37,800 m^3/day (10 mgd)		378,000 m^3/day (100 mgd)	
Item	¢/m^3	¢/1000 gal	¢/m^3	¢/1000 gal
O&M cost	1.8	7.3	1.6	6.5
Capital cost	4.3	17.2	2.5	10.3
Total treatment cost	6.1	24.5	4.1	16.8

(thereby fixing the amount of induced air and thus fixing the air/water ratio) and to increase tower depth. These trade-offs are illustrated in Figure 122. Table 91 contains some typical total treatment costs for these options.

Table 91 and Figure 122 can provide some insight into the important trade-offs involved in using tower aeration to remove trihalomethanes. For example, assume an initial design choice of a 6.6-m (20-ft) tower with an air/water ratio of 100:1. If an identical target water quality could be achieved by using a 3.3-m (10-ft) tower with an air/water ratio of 300:1, the cost would be slightly higher—1.6/m^3 (6.2/1000 gal) as opposed to 1.3¢/m^3 (4.9/1000 gal).

Synthetic Adsorption Resins—Granular synthetic resins can be used for the adsorption of trihalomethanes (see Section VI, Subsection Synthetic Resins). Data presented in this subsection are for a special resin called Ambersorb® XE-340. Cost equations were derived from preliminary cost data provided by the company (F. Slejko, Rohm & Haas Co., personal communication, 1980). For this analysis, the

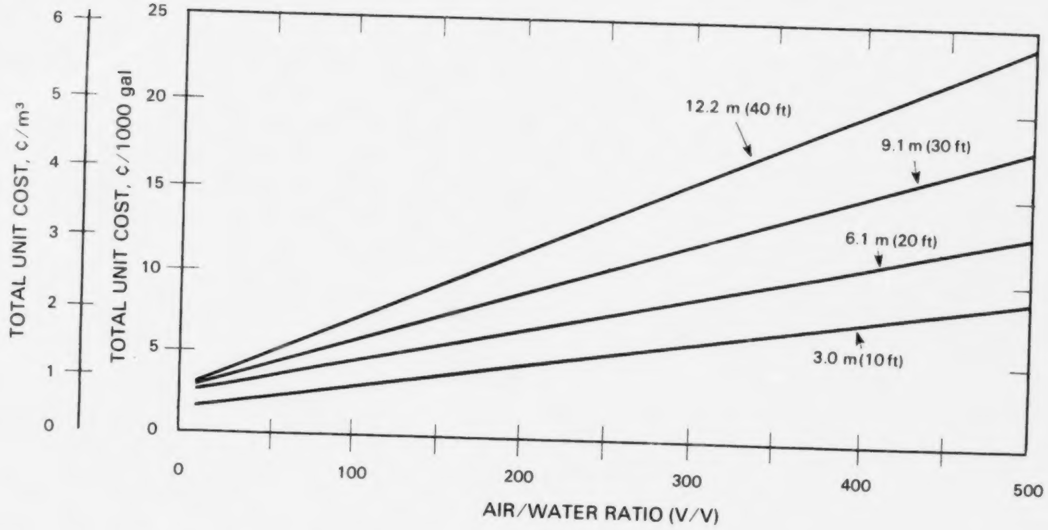

Figure 122. Total treatment unit costs of tower aeration for a 37,800-m³/day (10-mgd) system at various tower depths and air-to-water ratios.

TABLE 91. TOTAL TREATMENT COSTS OF ALTERNATIVE DESIGNS FOR A 37,800-m³/day (10-mgd) TOWER AERATION SYSTEM

Tower depth		Air/water ratio					
		100:1		300:1		500:1	
m	ft	¢/m³	¢/1000 gal	¢/m³	¢/1000 gal	¢/m³	¢/1000 gal
3.3	10	0.9	3.3	1.6	6.2	2.2	8.5
6.6	20	1.3	4.9	2.4	9.1	3.3	12.5
9.9	30	1.7	6.0	3.2	12.0	4.8	18.2
13.2	40	1.9	7.2	4.1	15.5	6.2	23.6

information has been based on 1977 costs updated to 1980 with the Construction Cost Index and the Producers Price Index (see Table 86). The data in Table 92 show the assumptions used in developing the Ambersorb® XE-340 costs. To calculate empty bed contact times (EBCT), specific design configurations were assumed for the two system sizes (Table 92).

TABLE 92. AMBERSORB® XE-340 ASSUMPTIONS

Item	Assumptions
Resin loss per regeneration	5 percent
Steam cost per regeneration	\$674.28/m³ (\$18.73/ft³) per reactivation
Solvent cost per regeneration	\$32.40/m³ (\$0.90/ft³) per reactivation
Quality control	\$9,000/yr
Resin cost	\$19.25/m³ (\$8.75/lb)
Resin density	605 kg/m³ (37 lb/ft³)
37,800-m³/day (10-mgd) system	6 Contactors at 8 m³ (289 ft³)/contactor
378,000-m³/day (100-mgd) system	20 Contactors at 24 m³ (862 ft³)/contactor

The interrelation of EBCT, time between regeneration, and total costs for treatment with Ambersorb® XE-340 for the two system sizes is shown in Figures 123 and 124. Table 93 presents O&M, capital, and total treatment costs for the two system sizes with an EBCT of 4 minutes, a regeneration frequency of once every 3 months, and an average operating capacity of 70 percent. Note that costs for disposal of the condensate are not included.

Removal of Trihalomethane Precursors—

Clarification—One technique for reducing the formation of trihalomethanes in water is to lower the concentration of trihalomethane precursors. Treatment techniques such as coagulation-sedimentation-filtration (conventional treatment), direct filtration, and precipitative softening may be employed in this manner (see Section VII, Subsection Clarification). Table 94 lists the unit processes assumed in each of these treatment trains, and Table 95 contains some of the assumptions used in generating the costs for them.[186] Total treatment cost curves are shown in Figure 119 for all these types of treatment plants, calculated for capacities from 3,780 to 567,000 m³/d (1–150 mgd). Tables 96, 97, and 98 contain O&M, capital, and total treatment costs for the two system sizes operating at an average 70-percent capacity. Note that free chlorination is included in these costs.

The costs listed in Tables 96, 97, and 98 would apply if a new treatment plant were constructed and operated. In many locations, however, clarification plants already exist. As discussed in Section VII, Subsection Clarification, improving clarification and moving the point of chlorination from the source water to later in the treatment

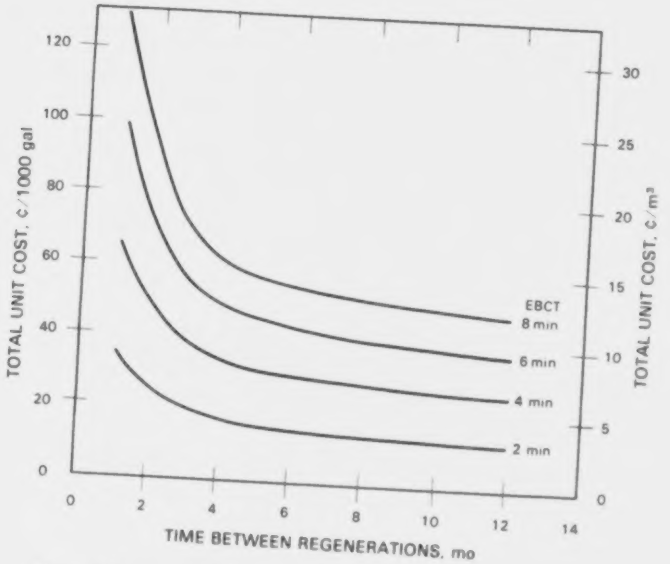

Figure 123. Total treatment unit costs vs. regeneration frequency for a 37,800-m³/day (10-mgd) Ambersorb® XE-340 system at various EBCT's.

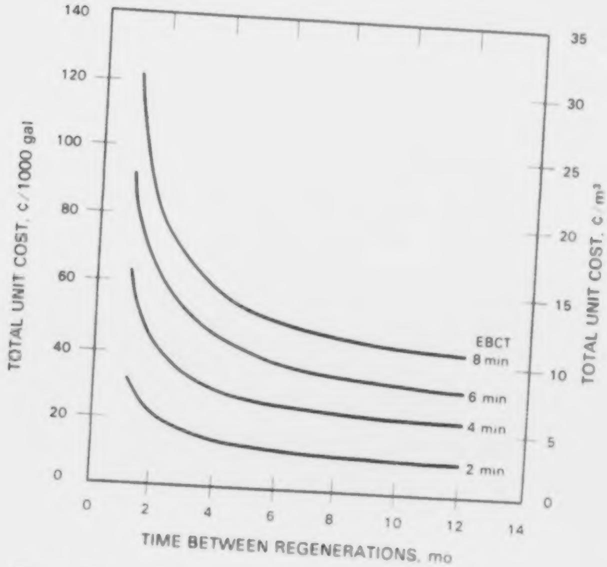

Figure 124. Total treatment unit costs vs. regeneration frequency for a 378,000-m³/day (100-mgd) Ambersorb® XE-340 system at various EBCT's.

TABLE 93. CAPITAL AND O&M COSTS FOR TREATMENT WITH AMBERSORB® XE-340[*]

Item	System treatment capacity			
	37,800 m³/day (10 mgd)		378,000 m³/day (100 mgd)	
	¢/m³	¢/1000 gal	¢/m³	¢/1000 gal
O&M cost	2.8	11.1	2.8	11.1
Capital cost	6.2	24.7	5.5	22.1
Total treatment cost	9.0	35.8	8.3	33.2

[*] Three-month regeneration frequency, 4-minute EBCT. Average operating capacity is 70 percent.

TABLE 94. UNIT PROCESSES ASSUMED IN EACH TREATMENT TRAIN

Direct filtration	Conventional treatment	Precipitative softening
Alum feed	Alum feed	Lime feed system
Polymer feed	Polymer feed	Chlorine feed[*]
Chlorine feed[*]	Chlorine feed[*]	Rapid mix
Rapid mix	Rapid mix	Upflow solids contact clarifier
Flocculation	Flocculation	Recarbonation basin
Gravity filtration	Sedimentation	CO_2 source
Hydraulic surface wash	Gravity filtration	Gravity filtration
Backwash pumping	Hydraulic surface wash	Hydraulic surface wash
Clearwell storage	Backwash pumping	Backwash pumping
Wash water surge basins	Clearwell storage	Clearwell storage
	Wash water surge basin	Wash water surge basin
		Sludge handling
		Lime recalcination

[*] Chlorine included in these unit processes.

TABLE 95. CLARIFICATION TREATMENT ASSUMPTIONS

Item	Dose	Assumed cost
Alum	15 mg/L, 25 mg/L	$0.08/kg ($70.00/ton)
Polymer	0.2 mg/L	$4.40/kg ($2.00/lb)
Chlorine	2 mg/L	$0.33/kg ($300.00/ton)
Lime	300 mg/L	$0.07/kg ($65.00/ton)
Natural gas	—	$0.014/sm³ ($0.0013/scf)
Diesel fuel	—	$0.17/L ($0.65/gal)

TABLE 96. CAPITAL AND O&M COSTS FOR DIRECT FILTRATION*

Item	System treatment capacity			
	37,800 m³/day (10 mgd)		378,000 m³/day (100 mgd)	
	¢/m³	¢/1000 gal	¢/m³	¢/1000 gal
O&M cost	2.5	9.6	0.9	3.5
Capital cost	3.9	14.9	1.7	6.4
Total treatment cost	6.4	24.5	2.6	9.9

*Chemical dose: Alum, 15 mg/L; polymer, 0.2 mg/L; chlorine, 2 mg/L. Average operating capacity is 70 percent.

TABLE 97. CAPITAL AND O&M COSTS FOR CONVENTIONAL TREATMENT*

Item	System treatment capacity			
	37,800 m³/day (10 mgd)		378,000 m³/day (100 mgd)	
	¢/m³	¢/1000 gal	¢/m³	¢/1000 gal
O&M cost	2.8	10.8	1.1	4.2
Capital cost	4.9	18.6	2.2	8.2
Total treatment cost	7.7	29.4	3.3	12.4

*Chemical dose: Alum, 25 mg/L; polymer, 0.2 mg/L; chlorine, 2 mg/L. Average operating capacity is 70 percent.

TABLE 98. CAPITAL AND O&M COSTS FOR PRECIPITATIVE SOFTENING*

Item	System treatment capacity			
	37,800 m³/day (10 mgd)		378,000 m³/day (100 mgd)	
	¢/m³	¢/1000 gal	¢/m³	¢/1000 gal
O&M cost	4.8	18.5	3.3	12.5
Capital cost	6.6	25.0	2.5	9.6
Total treatment cost	11.4	43.4	5.8	22.2

*Chemical dose: Lime, 300 mg/L; chlorine, 2 mg/L. Average operating capacity is 70 percent.

train will, in many cases, improve trihalomethane precursor removal. This step is a potentially inexpensive approach to trihalomethane control. Because changing coagulant dose or type (or both) and moving the chlorination point involves little or no capital expenditure, treatment costs for these techniques would be very low. Furthermore, applying the chlorine at a point in the treatment train where the disinfectant demand is lower than in the source water may permit lower doses to be used to achieve the same residual, thereby actually reducing overall treatment cost.[82,187]

Figures 125, 126, and 127 show the sensitivity of cost to changes in coagulant dose for clarification and in lime for precipitative softening, for 37,800- and 378,000-m³/day (10- and 100-mgd) plants at 70-percent capacity.

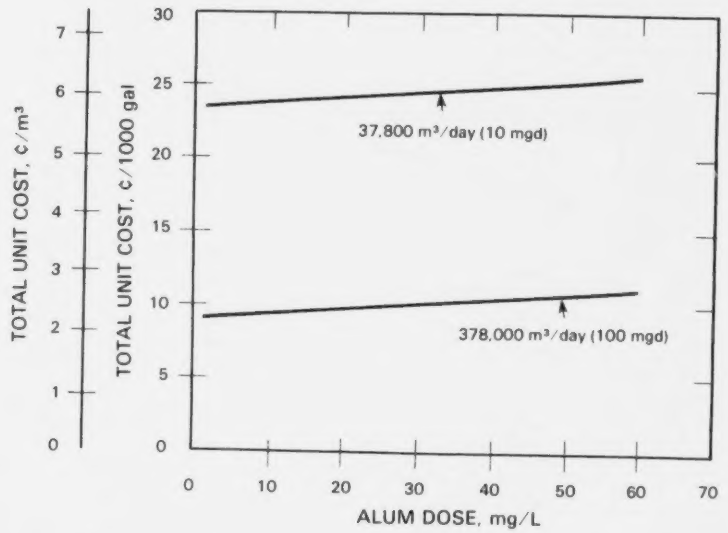

Figure 125. Total treatment unit costs of clarification by direct filtration vs. alum dose.

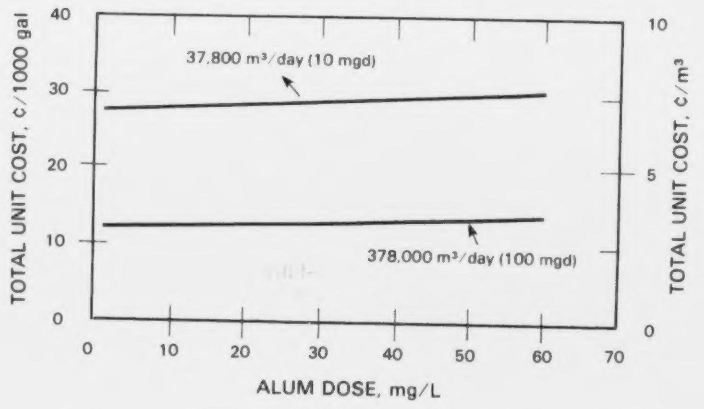

Figure 126. Total treatment unit costs of clarification by conventional treatment vs. alum dose.

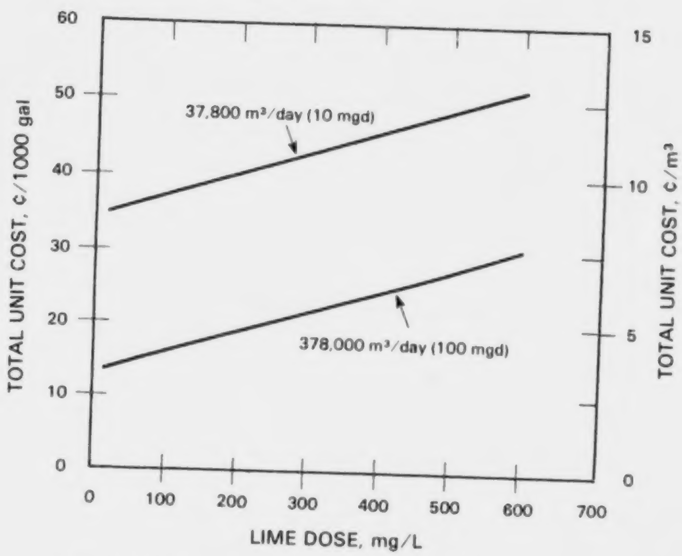

Figure 127. Total treatment unit costs of clarification by precipitative softening vs. lime dose.

Granular Activated Carbon Adsorption—As discussed in Section VII, Subsection Granular Activated Carbon, GAC adsorption is effective for trihalomethane precursor removal. For this analysis, two types of GAC systems will be considered.[188,189] One system uses activated carbon in separate contactors after sand filters (hereafter called "post-filter adsorbers"), and the other uses GAC as a replacement for the media in existing filter beds (hereafter called "sand replacement"). Both systems will be considered with onsite thermal reactivation. The need to consider the cost of separate GAC contactors is eliminated if GAC is assumed to replace sand in existing filters.

For purposes of the sand replacement analysis, a water treatment plant is assumed to consist of an integral number of 3,780-m^3/day (1-mgd) filters. Design parameters assumed for the sand replacement systems are listed in Table 99, and design assumptions for post-filter adsorption systems are presented in Table 100. Note that for sand replacement systems, a GAC loss of 10 percent/reactivation cycle is assumed, but a GAC loss of only 6 percent/reactivation cycle is assumed for post-filter adsorbers. These two assumptions are intended to reflect differences in the operation of the two systems. Sand replacement systems are labor intensive and increase the possibility of GAC loss because the activated carbon is changed manually and frequently backwashed. In post-filtration systems, fewer possibilities exist for handling losses, because the activated carbon is assumed to be changed hydraulically and is seldom backwashed between reactivation cycles.

Figures 128 through 131 present total treatment cost curves for both 37,800-m^3/day and 378,000-m^3/day (10- and 100-mgd) sand replacement and post-filter adsorption systems. Table 101 (page 244) contains O&M, capital, and total treatment costs for both systems operating at an average 70-percent capacity.

Powdered Activated Carbon Adsorption—PAC has been suggested for removal of trihalomethane precursors (see Section VII, Subsection Adsorption), and PAC costs have been developed for such an application. The PAC systems were sized for

TABLE 99. DESIGN PARAMETERS ASSUMED FOR GAC SAND REPLACEMENT SYSTEMS

Item	Assumption
Activated carbon cost	$1.54/kg ($0.70/lb)
Activated carbon loss per reactivation cycle	10 percent
Fuel cost	0.17¢/million joules ($1.80/million BTU)
Volume per filter	24 m^3 (856 ft^3)
Loss in adsorptive capacity	0 percent
Hearth loading	354 kg/day/m^2 (70 lb/day/ft^2)

TABLE 100. DESIGN PARAMETERS ASSUMED FOR GAC POST-FILTER ADSORBERS

Item	Assumption
Activated carbon cost	$1.54/kg ($0.70/lb)
Activated carbon loss per reactivation cycle	6 percent
Fuel cost	0.17¢/million joules ($1.80/million BTU)
Hearth loading	354 kg/day/m^2 (70 lb/day/ft^2)
Adsorber configuration:	
37,800-m^3/day (10-mgd) plant:	
No. of adsorbers	8
Diameter of adsorber	3.7 m (12 ft)
Vol./adsorber	41 m^3 (1,470 ft^3)
378,000-m^3/day (100-mgd) plant:	
No. of adsorbers	28
Diameter of adsorber	6.1 m (20 ft)
Vol./adsorber	122 m^3 (4,396 ft^3)
Loss in adsorptive capacity per reactivation cycle	0 percent

feeding an 11-percent slurry by weight. The 11-percent slurry is assumed to be stored and continuously mixed in uncovered concrete tanks that are placed below ground level, except for the top foot or so. For feed capacities of less than 320 kg/hr (700 lb/hr), 8 days of storage in two equal-size basins are included. For greater feed rates, 2 days of storage in a single basin are included. Mixers were sized based on a G value of 600/sec^{-1}. Storage/mixing basins include equipment for PAC feed from bags in smaller installations and from trucks or railroad cars in larger installations.

Energy requirements are based on the rated horsepower of a pump motor for continuous mixing of the 11-percent carbon slurry at a G value of 600/sec^{-1}. PAC requirements were estimated for various configurations. Labor requirements for the mixing/storage basin are 30 min/day per basin for inspection and routine maintenance, and 16 hr/year per basin for cleaning and gearbox oil change. Slurry pumps require 1 workhour/day per pump. Figure 132 (page 244) shows the total costs for PAC treatment at PAC concentration ranges of 5 to 45 mg/L and for five different system capacities. Table 102 (page 245) contains O&M, capital, and total treatment costs for 37,800- and 378,000 m^3/day (10- and 100-mgd) systems feeding 25 mg/L PAC and operating at an average 70-percent capacity.

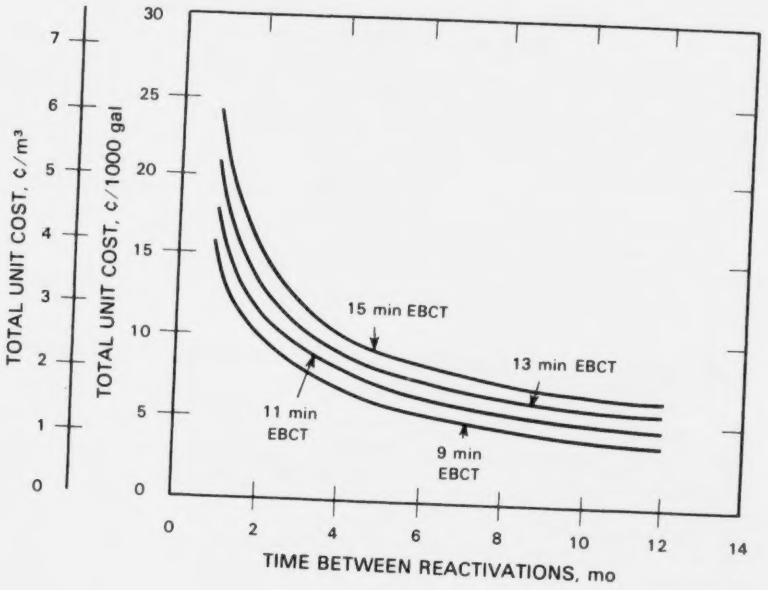

Figure 128. Total treatment unit costs vs. reactivation frequency for a 37,800-m³/day (10-mgd) GAC sand replacement system at various EBCT's.

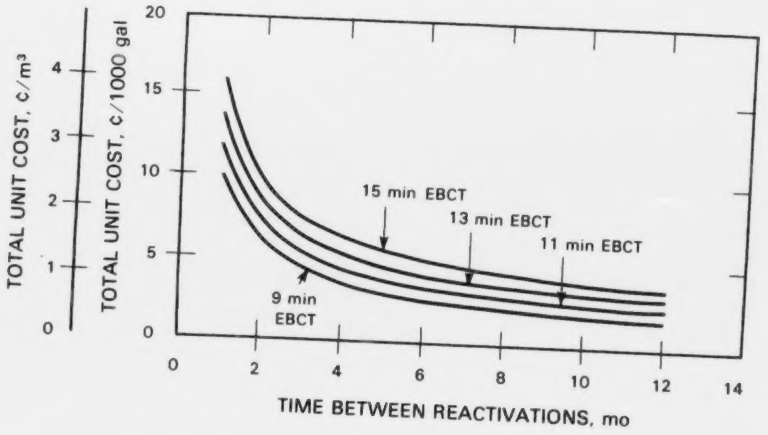

Figure 129. Total treatment unit costs vs. reactivation frequency for a 378,000-m³/day (100-mgd) GAC sand replacement system at various EBCT's.

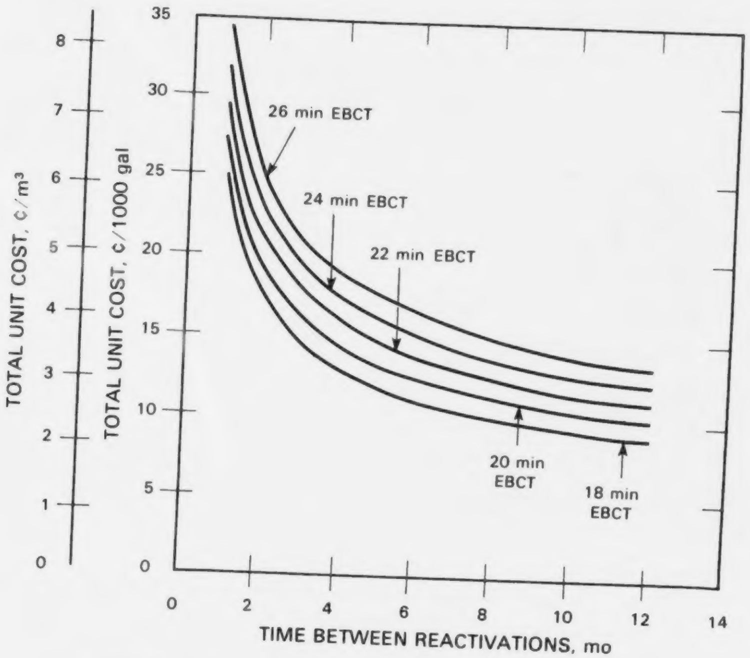

Figure 130. Total treatment unit costs vs. reactivation frequency for a 37,800-m³/day (10-mgd) GAC post-filter adsorber at various EBCT's.

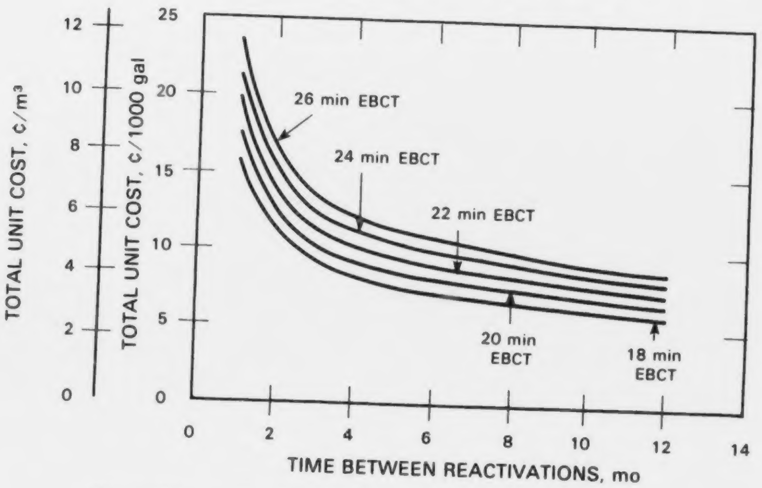

Figure 131. Total treatment unit costs vs. reactivation frequency for a 378,000-m³/day (100-mgd) GAC post-filter adsorber at various EBCT's.

TABLE 101. CAPITAL AND O&M COSTS FOR GAC ADSORPTION

Item	System treatment capacity			
	37,800 m³/day (10 mgd)		378,000 m³/day (100 mgd)	
	¢/m³	¢/1000 gal	¢/m³	¢/1000 gal
Sand replacement system:*				
O&M cost	0.8	3.1	0.7	2.6
Capital cost	1.3	5.0	0.6	2.1
Total treatment cost	2.1§	8.1§	1.3§	4.7§
Post-filter adsorber:†				
O&M cost	0.8	3.0	0.6	2.5
Capital cost	2.1	8.1	1.2	4.7
Total treatment cost	2.9§	11.1§	1.8§	7.2§

*Nine-minute EBCT, 3-month reactivation frequency, 10-percent loss/reactivation. Average operating capacity is 70 percent.

†Eighteen-minute EBCT, 6-month reactivation frequency, 6-percent loss/reactivation. Average operating capacity is 70 percent.

§The reader is reminded that these costs were calculated using a reactivation furnace hearth loading of 354 kg/d/m² (70 lb/d/ft²).[180] Previous reports used a value of 202 kg/d/m² (40 lb/d/ft²).[184] Using this lower value raises these costs 16 percent for both of the 37,800-m³/d (10-mgd) systems, 11 percent for the 378,000-m³/d (100-mgd) sand replacement system and 4 percent for the 378,000-m³/d (100-mgd) post-filter adsorber system.

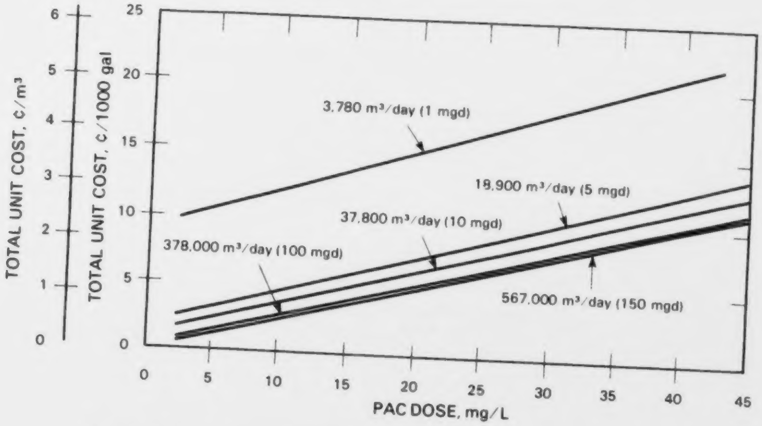

Figure 132. Total treatment unit costs for PAC treatment vs. PAC dose for different plant capacities.

Ozone Plus Granular Activated Carbon Adsorption—As shown earlier in this section under Granular Activated Carbon Adsorption, reactivation frequency has an important impact on the cost of GAC operation. GAC in combination with another unit process that helps lengthen the time between reactivations might result in a less expensive system.

Costs for a hypothetical system in which ozone is combined with a 378,000-m³/day (100-mgd) post-filter adsorber are shown in Figure 133. If the system is operating initially at point "P_1" without ozone (2 months between reactivations), then the addition of 2 mg/L ozone would have to increase the time between reactivations to "P_2"

TABLE 102. CAPITAL AND O&M COSTS FOR PAC TREATMENT*

	System treatment capacity			
	37,800 m³/day (10 mgd)		378,000 m³/day (100 mgd)	
Item	¢/m³	¢/1000 gal	¢/m³	¢/1000 gal
O&M cost	1.7	6.9	1.6	6.4
Capital cost	0.2	0.7	0.1	0.2
Total treatment cost	1.9	7.6	1.7	6.6

*PAC dose is 25 mg/L. Assumed cost for PAC is $0.66/kg ($600/ton). Average operating capacity is 70 percent.

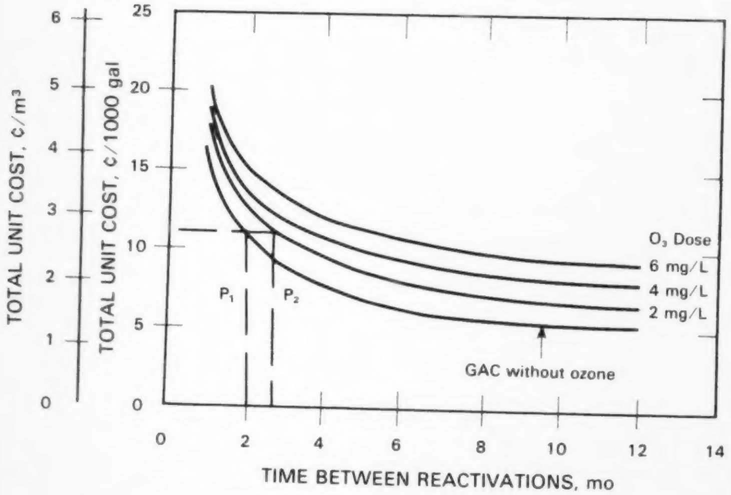

Figure 133. Total treatment unit costs for ozone plus GAC treatment vs. reactivation frequency for various ozone doses.[189]

(2.8 months) to break even on total treatment cost. The data in Table 103 show the increase in time between reactivations needed to break even on total treatment cost for various ozone dosages. These data were calculated for a system operating at a reactivation frequency of once every 2 months without ozone.

Ozone plus Ultra-violet Radiation—The combination of ozone and ultra-violet radiation (O_3/UV) is a new treatment technology. Results of a recent research project are presented in this subsection, and no attempt has been made to extrapolate the available costs beyond these results.[40] This study found that the process was effective in the removal of trihalomethanes and trihalomethane precursors (see Section VI, Subsection Ozone/Ultra-Violet Radiation and Section VII, Subsection Ozone/Ultra-Violet Radiation). Representative costs developed by an engineering consultant working on the project are presented in Table 104.

Anion Exchange—Anion exchange has proven effective for removing most of the organic trihalomethane precursors and thereby preventing the formation of trihalomethanes, (see Section VII, Subsection Ion Exchange). To calculate costs for

TABLE 103. REACTIVATION FREQUENCY REQUIRED TO OFFSET COST OF ADDING OZONE

Ozone dosage, mg/L	Break-even point,* months
0	2
2	2.8
4	3.7
6	5

*Total treatment cost.

TABLE 104. RANGE OF O_3/UV COSTS FOR TRIHALOMETHANE PRECURSOR REMOVAL[40]

	System treatment capacity			
	37,800 m³/day (10 mgd)		378,000 m³/day (100 mgd)	
Item	¢/m³	¢/1000 gal	¢/m³	¢/1000 gal
Ozone from O_2:				
O&M cost	1.4 - 2.0	5.4 - 7.8	1.3 - 2.0	5.2 - 7.9
Capital cost	0.3 - 0.5	1.2 - 2.1	0.3 - 0.5	1.1 - 2.0
Total treatment cost	1.7 - 2.5	6.6 - 9.9	1.6 - 2.5	6.3 - 9.9
Ozone from air:				
O&M cost	1.5 - 2.4	6.1 - 9.4	1.5 - 2.1	5.8 - 8.4
Capital cost	0.5 - 1.1	2.0 - 4.4	0.5 - 1.0	1.9 - 3.9
Total treatment cost	2.0 - 3.5	8.1 - 13.8	2.0 - 3.1	7.7 - 12.3

this type of treatment, two configurations were assumed: 1) a 37,800-m³/day (10-mgd) plant with one 41-m³ (1470-ft³) contactor and 2) a 378,000-m³/day (100-mgd) plant with ten 41-m³ (1470-ft³) contactors. Assumptions used in developing the anion exchange costs are presented in Table 105. The interrelation of EBCT, regeneration frequency, and total treatment cost for the two system sizes is illustrated in Figures 134 and 135. O&M, capital, and total treatment costs for the two system sizes are presented in Table 106.

TABLE 105. ANION EXCHANGE ASSUMPTIONS

Item	Assumption
Resin loss per regeneration	5 percent
Quality control	$9,000/yr
Resin cost	$6,480/m³ ($180/ft³)
Resin density	736 kg/m³ (45 lb/ft³)
Regeneration conc. (NaOH)	4 percent
Regenerate quantity	65 kg NaOH/m³ (4 lb/ft³)
Sodium hydroxide cost	$0.22/kg ($200/ton)
Regeneration requirement	6,800 L/m³ (50 gal/ft³)
10 mgd	1 contactor at 41 m³ (1,470 ft³) per contactor
100 mgd	10 contactors at 41 m³ (1,470 ft³) per contactor

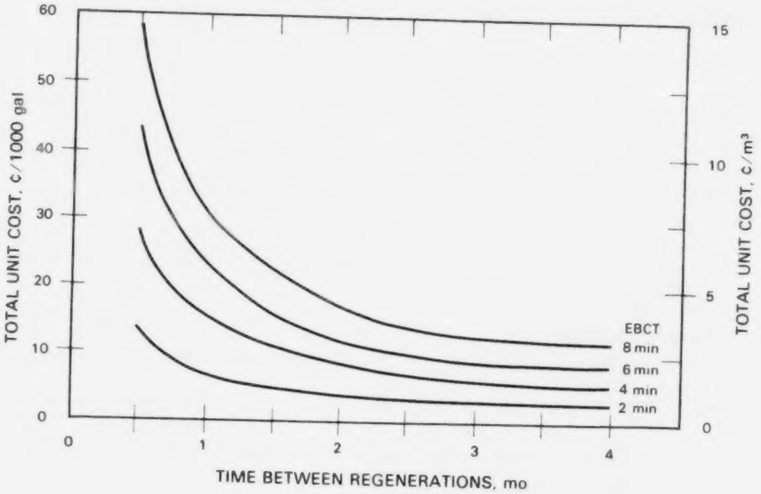

Figure 134. Total treatment unit costs vs. regeneration frequency for a 37,800-m³/day (10-mgd) anion exchange system at various EBCT's.

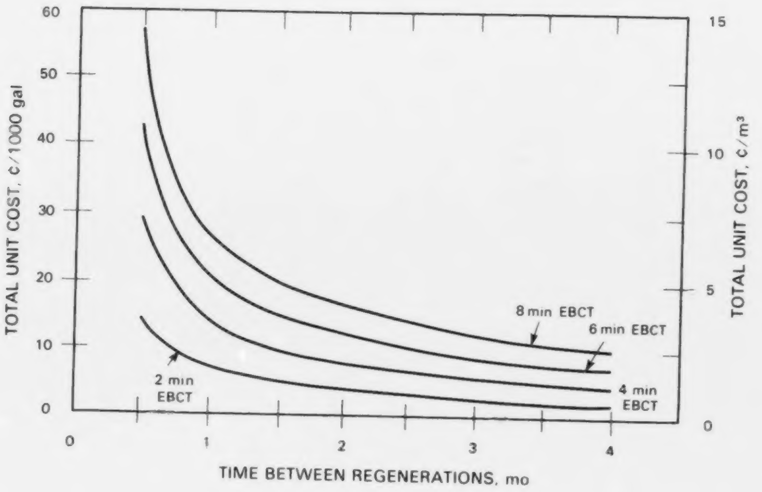

Figure 135. Total treatment unit costs vs. regeneration frequency for a 378,000-m³/day (100-mgd) anion exchange system at various EBCT's.

TABLE 106. CAPITAL AND O&M COSTS FOR ANION EXCHANGE*

Item	System treatment capacity			
	37,800 m^3/day (10 mgd)		378,000 m^3/day (100 mgd)	
	¢/m^3	¢/1000 gal	¢/m^3	¢/1000 gal
O&M cost	6.7	26.8	6.7	26.8
Captial cost	0.6	2.5	0.6	2.4
Total treatment cost	7.3	29.3	7.3	29.2

*Regeneration frequency, 2 weeks; EBCT, 4 minutes; loss/regeneration, 5 percent; average operating capacity, 70 percent.

Alternative Disinfectants—

Chlorine—The design variables unique to the cost computations for chlorination are shown in Table 107.[190]

Total treatment costs for chlorination versus chlorine dosage are depicted in Figures 136 and 137 for various sizes of plants with and without contact basins. O&M, capital, and total treatment costs for 37,800- and 378,000-m^3/day (10- and 100-mgd) plants are listed in Table 108.

TABLE 107. CHLORINATION ASSUMPTIONS

Item	Assumption
Cost of chlorine	$0.33/kg ($300/ton)
Chlorine dose	2 mg/L
Contact time (when used)	20 minutes

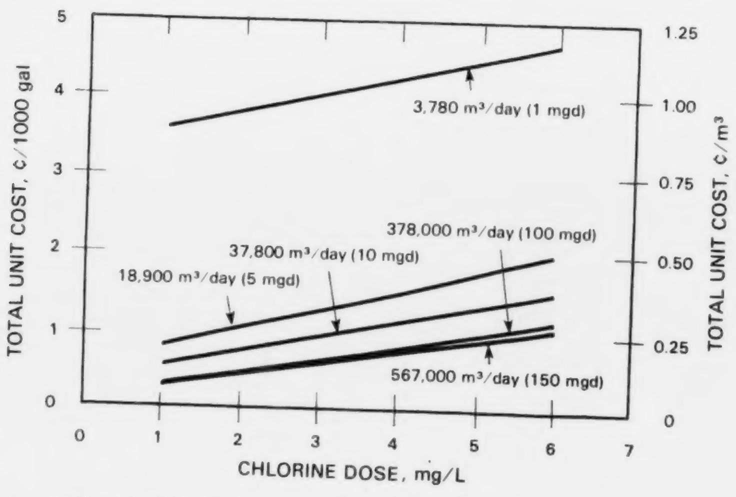

Figure 136. Total treatment unit costs for chlorination vs. chlorine dose for different plant capacities without contact basins.

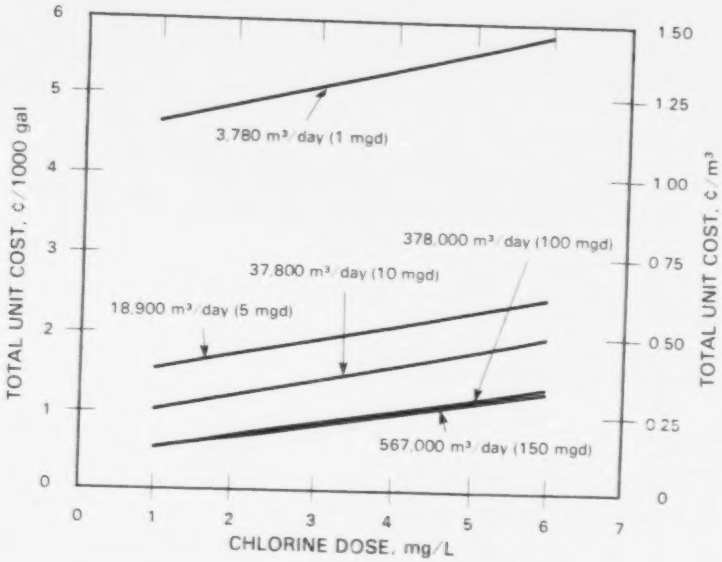

Figure 137. Total treatment unit costs for chlorination vs. chlorine dose for different plant capacities with contact basins.

TABLE 108. CAPITAL AND O&M COSTS FOR CHLORINATION*

	System treatment capacity			
	37,800 m³/day (10 mgd)		378,000 m³/day (100 mgd)	
Item	¢/m³	¢/1000 gal	¢/m³	¢/1000 gal
Chlorination				
w/o contact basin:				
O&M cost	0.2	0.6	0.1	0.3
Capital cost	0.1	0.2	<0.1	0.1
Total treatment cost	0.3	0.8	>0.1	0.4
Chlorination				
with contact basin:				
O&M cost	0.2	0.6	0.1	0.3
Capital cost	0.2	0.6	0.1	0.4
Total treatment cost	0.4	1.2	0.2	0.7

*Chlorine dose, 2 mg/L; operating at 70 percent of capacity on the average.

Chlorine Dioxide—The cost assumptions unique to chlorine dioxide are listed in Table 109.

To achieve equivalent disinfection results, the chlorine dioxide dose is assumed to be half that for chlorine; thus 1 mg/L of chlorine dioxide was assumed to achieve disinfection results equivalent to those achieved by 2 mg/L of chlorine. The data in Figures 138 and 139 show the total treatment costs for chlorine dioxide for various

TABLE 109. CHLORINE DIOXIDE ASSUMPTIONS

Item	Assumption
Chlorine	\$0.33/kg (\$300/ton)
Sodium chlorite ($NaClO_2$)	\$2.20/kg (\$2,000/ton)
Chlorine dioxide dose	1 mg/L
Contact time (when used)	20 minutes

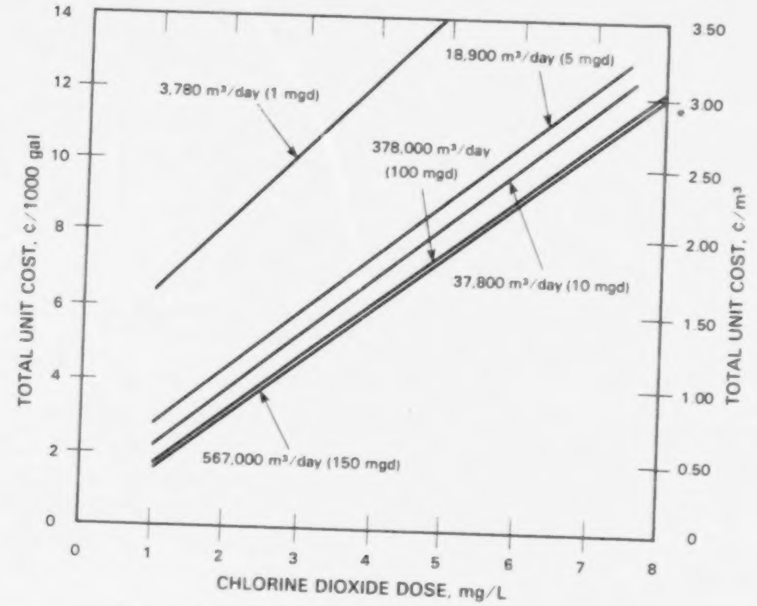

Figure 138. Total treatment unit costs for chlorine dioxide vs. chlorine dioxide dose for different plant capacities without contact basins.

sizes of systems with and without contact basins. O&M, capital, and total treatment costs for chlorine dioxide for 37,800- and 378,000-m^3/day (10- and 100-mgd) plants operating at an average 70-percent capacity appear in Table 110.

Ozonation—The cost of ozonation for various dosages and sizes of systems is shown in Figure 140. The data in Table 111 show O&M, capital, and total treatment costs for an ozone dose of 1 mg/L (assumed to be equivalent in disinfecting capacity to 2 mg/L of chlorine) for 37,800- and 378,000-m^3/day (10- and 100-mgd) systems operating at an average 70-percent capacity.

Chlorine-Ammonia Treatment (Combined Chlorine)—Combining ammonia with chlorine to form chloramines has been variously called the chloramine process, chloramination, and combined residual chlorination. The design assumptions for combined residual chlorination are shown in Table 112.

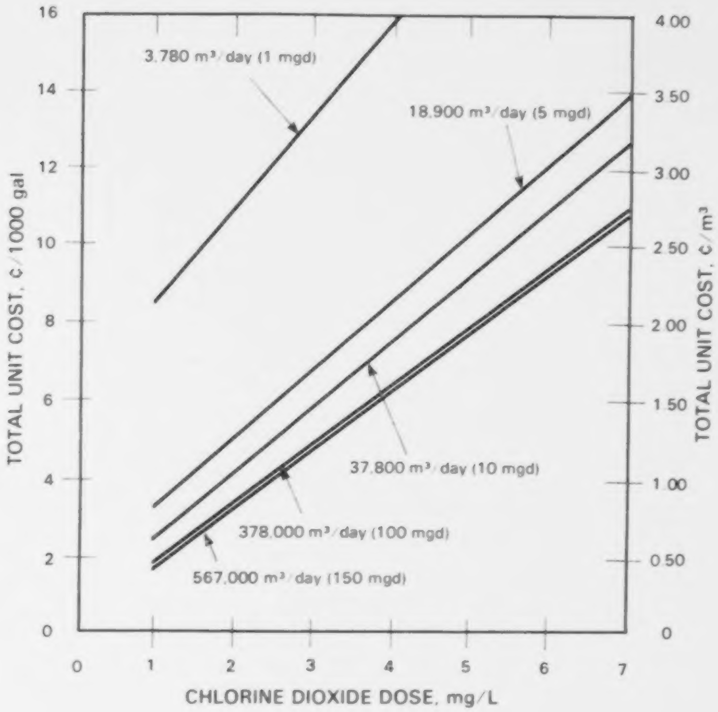

Figure 139. Total treatment unit costs for chlorine dioxide vs. chlorine dioxide dose for different plant capacities with contact basins.

TABLE 110. CAPITAL AND O&M COSTS FOR CHLORINE DIOXIDE*

	System treatment capacity			
	37,800 m³/day (10 mgd)		378,000 m³/day (100 mgd)	
Item	**¢/m³**	**¢/1000 gal**	**¢/m³**	**¢/1000 gal**
Chlorine dioxide without contact chamber:				
O&M cost	0.5	1.9	0.4	1.6
Capital cost	0.1	0.3	<0.1	0.1
Total treatment cost	0.6	2.2	<0.5	1.7
Chlorine dioxide with contact chamber:				
O&M cost	0.5	1.9	0.4	1.6
Capital cost	0.3	1.0	0.1	0.5
Total treatment cost	0.8	2.9	0.5	2.1

*Chlorine dioxide dose, 1 mg/L; average operating capacity, 70 percent

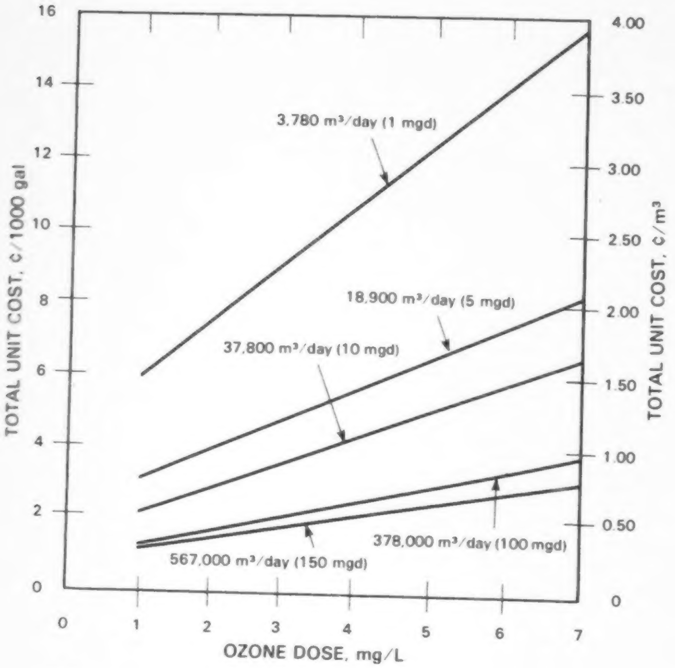

Figure 140. Total treatment unit costs for ozonation vs. ozone dose for different plant capacities.

TABLE 111. CAPITAL AND O&M COSTS FOR OZONE*

	System treatment capacity			
	37,800 m³/day (10 mgd)		378,000 m³/day (100 mgd)	
Item	¢/m³	¢/1000 gal	¢/m³	¢/1000 gal
O&M cost	0.2	0.7	0.1	0.4
Capital cost	0.4	1.5	0.3	0.8
Total treatment cost	0.6	2.2	0.4	1.2

*Ozone dose, 1 mg/L; contact time, 10 minutes; average operating capacity, 70 percent.

TABLE 112. COMBINED RESIDUAL CHLORINATION ASSUMPTIONS

Item	Assumption
Chlorine	$0.33/kg ($300/ton)
Ammonia	$0.22/kg ($200/ton)
Ratio of chlorine to ammonia	3:1
Chloramine dose	3 mg/L
Contact time (when used)	20 minutes

Total treatment costs of combined residual chlorination for various chloramine dosages and sizes of plants with and without contact basins are shown in Figures 141 and 142. O&M, capital, and total treatment costs for 37,800- and 378,000-m^3/day (10- and 100-mgd) plants appear in Table 113.

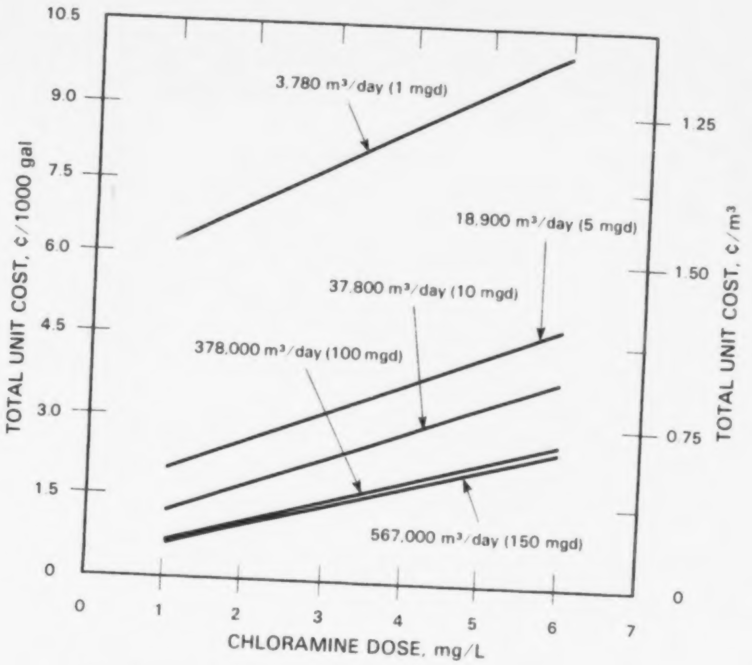

Figure 141. Total treatment unit costs of chlorine-ammonia treatment vs. chloramine dose for different plant capacities without contact basins.

Discussion—

The cost analyses in this section have shown the impact of several variables on the amortized capital and O&M costs for the unit processes that might be used for the control of trihalomethane concentrations in drinking water. Because the different unit processes have different objectives and different efficiencies in achieving these objectives, treatment costs can only be compared on the basis of equal performance. For example, to compare tower aeration with the use of PAC adsorption for a given percentage of trihalomethane removal, Figure 25 would be used to estimate the air/water ratio needed, and Figure 29 would be used to estimate the PAC dosage needed. Then Figures 121 and 132 would be used to obtain the treatment cost for that air/water ratio and PAC dosage, respectively. Thus, by combining these cost figures with the discussions on effectiveness presented in Sections VI–VIII, water utility personnel, design engineers, and others should be able to assess the relative costs associated with a given unit process.

Water treatment processes as typically employed exhibit highly variable efficiencies. Within the above limitations, a summary of total unit treatment costs has

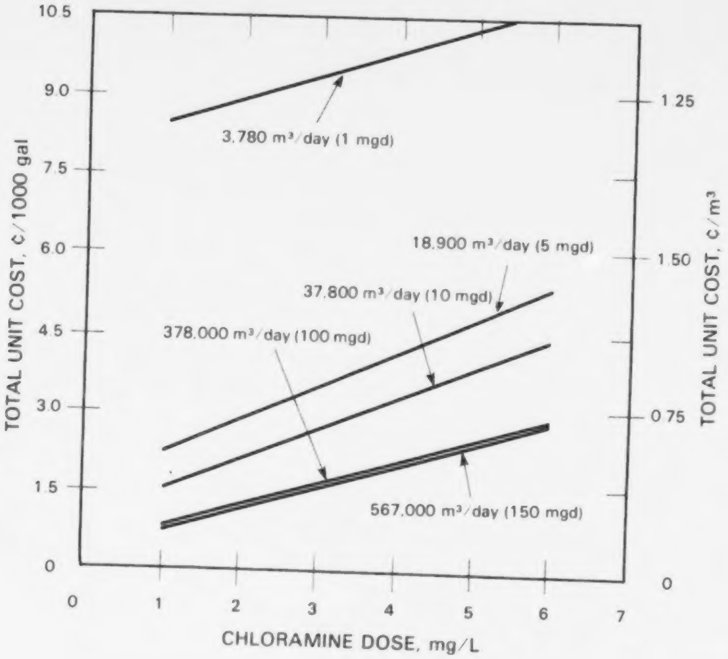

Figure 142. Total treatment unit costs of chlorine-ammonia treatment vs. chloramine dose for different plant capacities with contact basins.

TABLE 113. CAPITAL AND O&M COSTS FOR COMBINED RESIDUAL CHLORINE*

Item	System treatment capacity			
	37,800 m³/day (10 mgd)		378,000 m³/day (100 mgd)	
	¢/m³	¢/1000 gal	¢/m³	¢/1000 gal
Ammoniation w/o contact basin:				
O&M cost	0.5	1.8	0.3	1.3
Capital cost	0.2	0.6	0.1	0.2
Total treatment cost	0.7	2.4	0.4	1.5
Ammoniation with contact basin:				
O&M cost	0.5	1.8	0.3	1.3
Capital cost	0.2	0.9	0.1	0.5
Total treatment cost	0.7	2.7	0.4	1.8

*Combined chlorine dose, 3 mg/L; average operating capacity, 70 percent.

been prepared (Table 114, Section XI) for each of the unit processes using a set of conditions for the key variables that will produce equal effectiveness. The choice of unit process would depend largely on the degree of the trihalomethane problem at a particular utility. Process effectiveness varies greatly with the key variable assumed.

SECTION XI
SUMMARY OF TREATMENT CONSIDERATIONS

Three approaches have been investigated for trihalomethane control: removal of trihalomethanes, removal of trihalomethane precursors, and the use of disinfectants other than free chlorine. Of these, the use of alternative disinfectants appears to be the most effective and the least costly. Chlorine dioxide, ozone, and chloramines produce no significant concentrations of trihalomethanes when used as disinfectants. Theoretically, any utility with any trihalomethane precursor concentration could reduce its instantaneous trihalomethane (InstTHM) concentration to almost zero by the use of one of these three disinfectant alternatives to free chlorine. Furthermore, the cost of any of these unit processes, calculated either with or without contact chambers, is very low (Tables 110, 111, and 113).

The major disadvantage of this approach to trihalomethane control is that it does not remove trihalomethane precursors. Although no trihalomethanes will be produced as disinfection byproducts, other byproducts will still be produced as the oxidants (disinfectants) react with organic matter in the water. Further, some of these byproducts will be halogenated if chlorine dioxide or chloramines are used as the disinfectant alternative. Additionally, each of the disinfectants has inherent disadvantages. For example, ozone does not produce a residual for the distribution system, chloramine is a weaker disinfectant than free chlorine and may itself have some unique toxicologic properties,[168,169] and chlorine dioxide produces chlorite and chlorate as inorganic byproducts, anionic species whose health effects are currently unknown.[71,146] Because of the cost advantages, a water utility requiring trihalomethane control probably would consider the use of alternative disinfectants as the first approach to meeting the Trihalomethane Regulation,[3] but utility managers and their consultants should also consider the above disadvantages of this approach.

Alternatively, nine approaches to the control of trihalomethanes by removal of trihalomethanes and trihalomethane precursors were studied: oxidation, aeration, adsorption, clarification, ion exchange, biodegradation, pH adjustment, source control, and intense mixing during disinfection. Within these nine approaches, 19 different techniques were examined. Several of these techniques were not extensively tested for this purpose: oxidation by ozone plus ultraviolet radiation and by hydrogen peroxide, adsorption by Ambersorb® XE-340, ion exchange by strong- and weak-base resins, biodegradation, and intense mixing during disinfection. Although some of these techniques were effective, they will not be discussed further because design considerations are less amenable for immediate application.

One of the remaining 12 techniques to be compared for treatment effectiveness and relative cost is source control. Source control is, however, a nontreatment process and cannot be compared on an equal basis with the other unit processes. Obtaining the best quality source water is of paramount importance and should be a goal of all water utility managers and consulting engineers. Examination of the source for possible improvement with respect to trihalomethane precursor concentration is always important in the analysis of any water utility's practices.

Summary of Treatment Effectiveness and Costs*

Table 114 compares the performance and costs of the remaining 11 unit processes: oxidation by ozone, chlorine dioxide, and potassium permanganate; aeration by diffused air and with aeration towers; adsorption by powdered activated carbon and granular activated carbon; clarification by coagulation-settling-filtration, precipitative softening, and direct filtration; and the lowering of pH. This table summarizes the behavior of these unit processes with respect to several common areas: the effect on trihalomethane precursor concentrations, the effect on trihalomethane concentrations, the formation of other byproducts, the effect on disinfection, and representative estimated costs.

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* All costs are rounded to two significant figures.

For this table, the representative estimated costs were calculated for a single treatment plant size, 378,000 m^3/d (100 mgd), at three levels of treatment success and were based on the cost of chemical dosages and of other operating parameters that achieved specified levels of treatment. These data were collected at specific utilities studied and reported in Sections VI–X. These data should be used for comparison purposes of costs for equal treatment and should *not* be considered universally applicable. Absolute effectiveness of unit processes and costs will vary among locations. This summary table draws together the most important features of all of the processes listed for control of trihalomethanes by removal of trihalomethanes and trihalomethane precursors and should allow the comparison of these processes on an approximately equal basis.

Examples of Treatment Options

To assist water utility managers, consulting engineers, and others in assessing treatment options, *some* treatment possibilities for the following four systems[*] will be discussed:

1) a 37,800-m^3/d (10-mgd) groundwater system with chlorination only, having an average InstTHM concentration in the distribution system[†] of 0.20 mg/L;

2) a similar-sized groundwater utility[†] with chlorination only, having an average InstTHM concentration in the distribution system of 0.12 mg/L;

3) a 378,000-m^3/d (100-mgd) utility treating surface water with conventional treatment, having an average InstTHM concentration in the distribution system of 0.20 mg/L; and

4) a 378,000-m^3/d (100-mgd) utility treating surface water with conventional treatment having an average InstTHM concentration in the distribution system of 0.12 mg/L.

For the purposes of these examples, the alternative of using a disinfectant other than free chlorine will not be discussed because that application is relatively straightforward. The reader is reminded, however, of the previously cited disadvantages to this approach.

The discussion of these examples will focus on trihalomethane and trihalomethane precursor removal options in an attempt to show how water utility managers, consulting engineers, and others can determine treatment effectiveness and estimate treatment costs as a first step to selecting the most reasonable options for pilot study at the actual location. Of course, many other treatment options are possible and should be considered in any actual case, but these examples should provide helpful guidance as to the proper approach. As noted in Table 114, each process has disadvantages, and, although they are not always mentioned in the following examples, they must not be overlooked.

1A) *37,800-m^3/d (10-mgd) Groundwater Utility 2 x MCL—0.15 mg/L InstTHM in Finished Water:*

For the first example, the smaller utility treating goundwater by chlorination only, with a relatively high InstTHM concentration (0.20 mg/L) in the distribution system, an approximate 50 percent lowering of the trihalomethane concentration in

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[*] The first three examples will be discussed for two different cases: (A) where a large percentage of the possible trihalomethane production has occurred rapidly at the treatment plant, and (B) where a large amount of the possible trihalomethane production occurs in the distribution system after the water has left the plant.

[†] For the purposes of these examples, these groundwater systems are assumed to have all the flow collected in one location.

TABLE 114. SUMMARY OF SALIENT FEATURES OF PRACTICAL AND EFFECTIVE PROCESSES FOR CONTROLLING TRIHALOMETHANES IN DRINKING WATER

Treatment	Precursor	Trihalomethanes	Other Byproducts
Ozone Oxidation	Good to very good destruction is technically feasible. The apparent concentration may increase at low doses. High doses and long contact times are required for good destruction, and complete destruction is difficult.	No effect by ozone, some incidental gas stripping.	Some are formed, but they will not contain chlorine, unless free chlorination or chlorine dioxide is employed. Bromine-containing THM **may** not be formed on later chlorination.
Chlorine Dioxide Oxidation	Good destruction is technically feasible, but complete destruction was not achieved.	No effect.	Some are formed by the process and some will contain halogen.
Potassium Permanganate Oxidation	Fair destruction is technically feasible, but complete destruction was not achieved.	No effect.	Some are formed by the process and some will contain halogen, if free chlorine or chlorine dioxide is used.
Lowering pH	Fair decline of TermTHM concentration is technically feasible. Affects the rate of reaction between free chlorine and precursor, thereby lowering resulting THM concentration.	No effect.	None formed by the process, but some formed during final disinfection.
Diffused-Air Aeration	No effect and THM will form if free chlorine is used.	Good to very good removal is technically feasible, but bromine-containing THMs are harder to remove than chloroform. High air to water ratios are difficult to achieve.	None are known to be formed by the process but some are still formed during disinfection. Byproducts will contain halogen if free chlorine or chlorine dioxide is used.
Tower Aeration	No effect and THM will form if free chlorine is used.	Good to very good removal is feasible, but bromine-containing THMs are harder to remove. High air to water ratios can be achieved.	None known to be formed by the process, but some are still formed during disinfection. Byproducts will contain halogen if free chlorine or chlorine dioxide is used.

Continued

TABLE 114. (Continued)

Disinfection	Representative estimated cost* for 378,000 m³/d (100 mgd) in ¢/m³ (¢/1000 gal)			Reference	Remarks
	20% removal	50% removal	80% removal		
	Caddo Lake water, TX, Precursor Removal				
Excellent, but no residual is created. Organisms may regrow in the distribution system.	.2 mg/L 0.48 (1.8)*	20 mg/L 2.1 (7.9)*	50 mg/L 4.0 (15)*	Fig. 75 Fig. 140	Slightly better at high pH.
	—with contact chambers—				
	Ohio River water, precursor removal				
Good and provides a residual. Slightly more effective at higher pH.	Not determined	8 mg/L 3.2 (12)* w/o contact chambers	Not achieved	Fig. 78 Fig. 138	Residual oxidant should be limited to 0.5 mg/L because of health effect.
	Ohio River water, precursor removal				
Poor; a disinfectant must be used.	10 mg/L for 10 hours 2.6 (10)* w/o contact chamber	Not achieved	Not achieved	Table 41	Pink water with overdose. Better at high pH.
	Daytona Beach, FL, precursor removal				
Free chlorine is more effective at lower pH.	0.9 pH unit 19%† Equiv. of 2 mg/L H_2SO_4 0.03 (0.12)*	Not achieved	Not achieved	Table 45	May cause some corrosion problems.
	Cincinnati, OH, tap water, THM removal				
A disinfectant is required.	A/W**=2:1 0.48 (1.8)*	A/W=8:1 1.3 (4.9)*	A/W=20:1 3.7 (14)*	Table 9 Fig. 120	Influent air can be cleaned. Possible air pollution problems. Removes regulated contaminant. Some removal of SOCs@ and T&O# compounds.
	North Miami Beach, FL, THM removal				
A disinfectant is required.	Not determined.	A/W=4:1 0.56 (2.1)*	A/W=32:1 0.78 (2.9)*	Table 12 Fig. 121	Difficult to clean air, may entrain particulates. Possible air pollution problems. Removes regulated contaminant. May have to protect from freezing. Some removal of SOCs@ and T&O# compounds.

TABLE 114. (Continued)

Treatment	Precursor	Trihalomethanes	Other Byproducts
Powdered Activated Carbon Adsorption	Good to very good removal is feasible. Removal is influenced by influent concentration and the loading is proportional to the influent concentration.	Good to very good removal is feasible. Bromine-containing THMs are better adsorbed than chloroform. Removal is influenced by influent concentration and the loading is proportional to the influent concentration.	None are formed by the process. Some removal of those coming to the process and less reformation as related to TOC removal. Will contain halogen if chlorine or chlorine dioxide is used.
Granular Activated Carbon Adsorption	Good to very good removal technically feasible. Removal is nearly complete when adsorbent is fresh, then breakthrough **toward** exhaustion begins. Complete exhaustion generally does not occur, however. Loading is proportional to influent concentration and desorption may occur when the influent concentration declines.	Good to very good removal is technically feasible. Removal is nearly complete when adsorbent is fresh but then breakthrough to exhaustion occurs. Bromine-containing THMs adsorbed better than chloroform. Loading is proportional to influent concentration and desorption will occur if the influent concentration drops.	None formed by the process and some can be removed. Because of good TOC removal, fewer are formed during disinfection.

Continued

TABLE 114. (Continued)

	Representative estimated cost* for 378,000 m³/d (100 mgd) in ¢/m³ (¢/1000 gal)				
Disinfection	**20% removal**	**50% removal**	**80% removal**	**Reference**	**Remarks**
	Louisville, KY, tap water, THM removal				
Removes chlorine, so must post-disinfect. Some reduction in disinfectant demand	10 mg/L **0.74 (2.8)***	50 mg/L **3.4 (13)***	150 mg/L **10.3 (39)***	Table 16 Figure 132	Some removal of SOCs@ and T&O# compounds. No desorption with decreasing concentration because PAC only used once. Sludge disposal a problem.
	Ohio River water, precursor removal				
	9.5 mg/L Starting at 1 μmol/L **0.69 (2.6)***	43 mg/L Starting at 1 μmol/L **2.9 (11)***	222 mg/L Starting at 1 μmol/L **15 (57)***	Fig. 82 Fig. 132	
	Huntington, WV, THM removal				
Chlorine removed, so post-disinfection required. Disinfectant demand is lower than when TOC is removed.	7 min. EBCT§ 7 wks react. Sand replacem. **1.6 (6.0)***	7 min. EBCT§ 4 wks react. Sand replacem. **2.4 (9.0)***	7 min. EBCT§ 2 wks react. Sand replacem. **4.2 (16)***	Table 21 Ref. 18 Fig. 129	SOC@ & T&O# compounds also removed. Requires reactivation or replacement. Complete removal does not last long. Possible corrosion problems if effluent TOC‡ concentration near zero.
	Huntington, WV, precursor removal				
	7 min. EBCT§ 5.5 wks react. Sand replacem. **1.9 (7.1)***	7 min. EBCT§ 3 wks react. Sand replacem. **2.9 (11)***	7 min. EBCT§ 1 wk react. Sand replacem. **7.4 (28)***	Table 42 Ref. 18 Fig. 129	

TABLE 114. (Continued)

Treatment	Precursor	Trihalomethanes	Other Byproducts
Clarification By Coagulation, Sedimentation, Filtration	Good removal is feasible. If reaction with free chlorine is fast, delaying chlorination to after clarification will permit more removal. More removal will occur at lower pH but the reaction between free chlorine and precursor will be slower.	No effect.	None formed by the process and some may be removed. Because of TOC removal, fewer are formed later during disinfection. Some will contain halogen if free chlorine or chlorine dioxide is used.
Clarification By Precipitative Softening	Good removal is technically feasible. The faster reaction rate between free chlorine and precursor at higher pH should result in additional benefit by delaying chlorination.	No removal by process. Higher pH accelerates reaction to form THMs.	None formed by the process. Because of TOC removal, fewer are formed during disinfection. Some will contain halogen if free chlorine or chlorine dioxide is used.
Clarification By Direct Filtration	Good removal is technically feasible. THM concentrations will be lower if chlorination is delayed to after the process.	No effect.	None formed by the process. Because of TOC removal, fewer are formed during disinfection. Some will contain halogen if free chlorine or chlorine dioxide is used.

*All costs are rounded to two significant figures

†Actual percent removal at that location.

**A/W = Air to Water Ratio (Volume/Volume)

#T&O = Taste and Odor

@SOC = Synthetic Organic Contaminants

§EBCT = Empty Bed Contact Time (Empty Bed volume divided by flow rate)

‡TOC = Total Organic Carbon

TABLE 114. (Continued)

	Representative estimated cost* for 378,000 m^3/d (100 mgd) in ¢/m^3 (¢/1000 gal)				
Disinfection	**20% removal**	**50% removal**	**80% removal**	**Reference**	**Remarks**
		Precursor removal			
Disinfectant demand lower if disinfection is delayed.	Wheeling, WV 16%† Lime = 16 mg/L Ferric Sulfate = 8 mg/L **4.0 (15)***	Fox Chapel, PA 49%† Alum = 27 mg/L Lime = 17 mg/L **4.0 (15)***	Not achieved	Fig. 59 Ref. 18; Table 27 Ref. 18 Fig. 126	Sludge disposal problem. Iron salts may be somewhat better than alum.
		Precursor removal			
Effectiveness of free chlorine reduced at higher pH. Disinfectant demand will be lower if disinfection delayed.	Jefferson Parish, LA 16-25%† Lime = 60 mg/L Cationic polymer = 4 mg/L **5.8 (22)***	Daytona Beach, FL 41%† Lime = 225 mg/L Alum = 25 mg/L Polymer = 0.1 mg/L **5.6 (21)***	Not achieved	Table 32 Ref. 14 Fig. 127	Sludge disposal a problem.
		Bridgeport, CT, precursor removal			
Disinfectant demand lower if disinfection follows clarification.	Not determined	36-54%† Alum = 21 mg/L Polymer = 0.1 mg/L **2.6 (10)***	Not achieved	Table 35 Ref. 91 Fig. 125	Little sludge produced. May require polymers.

*All costs are rounded to two significant figures

†Actual percent removal at that location

**A/W = Air to Water Ratio (Volume/Volume)

#T&O = Taste and Odor

@SOC = Synthetic Organic Contaminants

§EBCT = Empty Bed Contact Time (Empty Bed volume divided by flow rate)

‡TOC = Total Organic Carbon

the distribution system would be required so that the average concentration of trihalomethanes in samples collected throughout the distribution system would be less than 0.10 mg/L. Because much of the source water precursor has been converted into trihalomethanes prior to leaving the treatment plant in this example (i.e., the InstTHM concentration in the *finished* water was 0.15 mg/L with an increase of 0.05 mg/L in the distribution system), aeration could be employed to remove these trihalomethanes. According to Table 114, a 20:1 air to water ratio for a diffused-air system, or a 32:1 air to water ratio for a tower aeration system, achieved 80 percent removal of the InstTHM at one location. This would produce an expected average InstTHM concentration of 0.03 mg/L leaving the plant [0.15-(0.8)(0.15)] = 0.03 and 0.08 mg/L (0.03 + 0.05) in the distribution system, less than the trihalomethane MCL.[3] An estimated added cost for these two systems would be 3.7¢/m^3 (14¢/1000 gal)* (Figure 120) and 1.2¢/m^3 (4.5¢/1000 gal)* (Figure 121), respectively, neglecting the cost of treating the air (filtering, scrubbing, and so forth).

1B) *37,800-m^3/d (10-mgd) Groundwater Utility—THM Concentration 2xMCL —0.01 mg/L InstTHM in Finished Water:*

Because a high percentage of the source water trihalomethane precursor has not been converted into trihalomethanes by the time the water leaves the treatment plant, some trihalomethane precursor removal process must be employed. Because only chlorination facilities are available at this example site, a treatment scheme with a minimum of construction should be considered first. Two possibilities are: 1) direct filtration for trihalomethane precursor removal or 2) granular activated carbon adsorption without any prior sedimentation. Approximately 50 percent removal of the trihalomethane precursor would be sufficient so that the average of the samples collected in the distribution system would be lower than 0.10 mg/L.

According to the data in Table 114, a coagulant dose of 21 mg/L of alum and 0.1 mg/L of polymer produced approximately 50 percent precursor removal by direct filtration at one location. Note that the water being treated at this location was a low turbidity surface water, but for this example the groundwater was assumed to behave similarly. The estimated added cost of such a process would be 6.6¢/m^3 (25¢/1000 gal) for this system, Figure 125. Correspondingly, using the data in Table 114 from one location, a granular activated carbon adsorber having a 7-minute EBCT with the activated carbon replaced or reactivated every 3 weeks would achieve 50 percent removal of trihalomethane precursor. On a throwaway basis, the added cost of such a process would be 34¢/m^3 (130¢/1000 gal). Using on-site reactivation, the added cost would be 4.2¢/m^3 (16¢/1000 gal) (Figure 130). Because the added cost of granular activated carbon adsorption with on-site reactivation is less than direct filtration for this example, granular activated carbon adsorption would be the first unit process among those discussed that would be investigated on a pilot-plant basis to determine specific operating criteria for that location.

2A) *37,800-m^3/d (10-mgd) Groundwater Utility—THM Concentration 1.2xMCL —0.05 mg/L InstTHM in Finished Water:*

For the second example, a 37,800-m^3/d (10-mgd) treatment plant with a groundwater source and chlorination only, whose average InstTHM concentration in the distribution system was 0.12 mg/L, only about a 20 percent decline of either trihalomethane or trihalomethane precursor concentrations would be needed to bring this water utility's drinking water into compliance. Therefore, because a significant portion of the source water trihalomethane precursor has been converted to InstTHM in the finished water, aeration could be considered for the removal of trihalomethanes. If the InstTHM concentration in the finished water were about 0.05 mg/L, an aeration device producing 50 percent removal might be adequate. This could be done with an air to water ratio of 8:1 for diffused air and 4:1 for aeration towers, according to Table 114, using data from one location. The added cost for these two unit processes for this size treatment plant would be 1.8¢/m^3 (6.9¢/1000 gal) (Figure 120) and 0.90¢/m^3 (3.4¢/1000 gal) (Figure 121) respectively, neglecting the cost of treating the air (filtering, scrubbing, and so forth).

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*All costs are rounded to two significant figures.

2B) *37,800-m^3/d (10-mgd) Groundwater Utility—THM Concentration 1.2xMCL —0.01 mg/L InstTHM in Finished Water:*

Because insufficient InstTHM is present in the finished water to make trihalomethane removal a useful option, about a 20 percent removal of trihalomethane precursor would be required. Lowering the pH, treatment with potassium permanganate, or treatment with about 4 mg/L of chlorine dioxide (estimated from Figure 78) would provide 20 percent removal of precursor, according to Table 114, using data from specific locations, and would only involve the construction of a contact basin and the use of chemical feeders. The added cost for these three processes would be: pH control, 0.2¢/m^3 (0.6¢/1000 gal),* potassium permanganate, 2.9¢/m^3 (11¢/1000 gal), and chlorine dioxide, 2.4¢/m^3 (9.0¢/1000 gal) (Figure 139). If chlorine dioxide oxidation were considered as an alternative, investigations would have to include a determination of the production of the inorganic byproducts chlorite and chlorate to compare with the *recommended* limit for total residual oxidants of 0.5 mg/L.

3A) *378,000-m^3/d (100-mgd) Surface Water Utility—THM Concentration 2xMCL—0.15 mg/L InstTHM in Finished Water:*

For the third example of a 378,000-m^3/d (100-mgd) conventional treatment plant using a surface water source and having an average InstTHM concentration of 0.20 mg/L in the distribution system, a 50 percent decline in precursor concentration should be sufficient to bring this utility into compliance. Although they could be considered, approaches that produce modest effects on the trihalomethane precursor concentration—improving clarification, moving the point of chlorination to the clarified water, lowering the pH, and oxidation with potassium permanganate—probably would not be adequate.

Because the InstTHM concentration in the finished water is high, 0.15 mg/L, trihalomethane removal should be considered. An aeration system operating at 80 percent removal should be sufficient to lower the InstTHM concentration to a value below the MCL.[3] Using data from one location, a diffused-air system at a 20:1 air to water ratio or an aeration tower at an air to water ratio of 32:1, costing an additional 3.7¢/m^3 (14¢/1000 gal) and 0.78¢/m^3 (2.9¢/1000 gal), respectively, neglecting the cost of air treatment (filtering, scrubbing, and so forth), might be adequate (Table 114).

3B) *378,000-m^3/d (100-mgd) Surface Water Utility—THM Concentration 2xMCL—0.01 mg/L InstTHM in Finished Water:*

Because the InstTHM concentration in the finished water was not high, the removal of trihalomethane precursors would be required. According to Table 114, either oxidation with ozone or chlorine dioxide or adsorption with powdered or granular activated carbon should be able to produce a 50 percent decline in trihalomethane precursor concentration. Using the conditions from given locations listed in Table 114, the added costs for these four processes are: ozone, 2.1¢/m^3 (7.9¢/1000 gal), chlorine dioxide, 3.2¢/m^3 (12¢/1000 gal), PAC, 2.9¢/m^3 (11¢/1000 gal), and GAC (sand replacement, on-site reactivation) 2.9¢/m^3 (11¢/1000 gal). Beyond the differences in cost, each process has disadvantages: Ozone produces other organic byproducts, chlorine dioxide produces other organic byproducts as well as chlorite and chlorate, disposal of sludge may be a problem with powdered activated carbon, and granular activated carbon requires replacement or reactivation (Table 114).

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*Calculated in a manner similar to chlorine dioxide, but using the appropriate chemical.

Decisions as to which processes to study on a pilot-plant basis at a given location should take all of these factors into account, but the least expensive treatment, ozone oxidation, would be the first choice.

4) *378,000-m^3/d (100-mgd) Surface Water Utility—THM Concentration 1.2xMCL:*

For the fourth example, a 378,000-m^3/d (100-mgd) utility having a conventional treatment plant, using a surface water source and producing an average InstTHM concentration of 0.12 mg/L in the distribution system, a decline in trihalomethane precursor concentration of only about 20 percent would be needed to bring the utility into compliance. Under these circumstances, techniques producing a modest removal of trihalomethane precursor—improving clarification, moving the chlorination point, adjusting pH, or adding some oxidant—should result in an acceptable average InstTHM concentration in the distribution system at a very modest cost (see Table 114).

These examples show how water utility personnel, design engineers, and Primacy Agencies might compare options when attempting to control the trihalomethane concentration at a given location. With diligent disinfection as the final treatment step and proper surveillance of the distribution system, any of these processes can be used for trihalomethane control with the knowledge that water with an acceptable bacteriologic quality will reach the consumer's tap. Of course, many other combinations of source water qualities, existing treatment processes, and treatment options can occur. This research report provides information concerning cost-effective treatment processes that can be considered by water utility personnel design engineers, and Primacy Agencies to successfully control the concentration of trihalomethanes in the Nation's drinking water while maintaining high bacteriologic water quality at the consumer's tap.

SECTION XII
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SECTION XIII
APPENDIX*

Accordingly, Part 141, Title 40 of the Code of Federal Regulations is hereby amended as follows:

1. By amending § 141.2 to include the following new paragraphs (p) through (t):

§ 141.2 Definitions

* * * * * * * * * *

(p) "Halogen" means one of the chemical elements chlorine, bromine or iodine.

(q) "Trihalomethane" (THM) means one of the family of organic compounds, named as derivatives of methane, wherein three of the four hydrogen atoms in methane are each substituted by a halogen atom in the molecular structure.

(r) "Total trihalomethanes" (TTHM) means the sum of the concentration in milligrams per liter of the trihalomethane compounds (trichloromethane [chloroform], dibromochloromethane, bromodichloromethane and tribromomethane [bromoform]), rounded to two significant figures.

(s) "Maximum Total Trihalomethane Potential (MTP)" means the maximum concentration of total trihalomethanes produced in a given water containing a disinfectant residual after 7 days at a temperature of 25°C or above.

(t) "Disinfectant" means any oxidant, including but not limited to chlorine, chlorine dioxide, chloramines, and ozone added to water in any part of the treatment or distribution process, that is intended to kill or inactivate pathogenic microorganisms.

2. By revising § 141.6 to read as follows:

§ 141.6 Effective dates.

(a) Except as provided in paragraph (b) of this section, the regulations set forth in this part shall take effect on June 24, 1977.

(b) The regulations for total trihalomethanes set forth in § 141.12(c) shall take effect 2 years after the date of promulgation of these regulations for community water systems serving 75,000 or more individuals, and 4 years after the date of promulgation for communities serving 10,000 to 74,999 individuals.

3. By revising the introductory paragraph and adding a new paragraph (c) in § 141.12 to read as follows:

§ 141.12 Maximum contaminant levels for organic chemicals.

The following are the maximum contaminant levels for organic chemicals. The maximum contaminant levels for organic chemicals in paragraphs (a) and (b) of this section apply to all community water systems. Compliance with the maximum contaminant levels in paragraphs (a) and (b) is calculated pursuant to § 141.24. The maximum contaminant level for total trihalomethanes in paragraph (c) of this section applies only to community water systems which serve a population of 10,000 or more individuals and which add a disinfectant (oxidant) to the water in any part of the drinking water treatment process. Compliance with the maximum contaminant level for total trihalomethanes is calculated pursuant to § 141.30.

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*From *Federal Register, 44*, No. 231, 28641-28642 (Nov. 29, 1979) as corrected by *Federal Register, 45*, No. 49, 15542-15547 (March 11, 1980).

* * * * * * * * * * * * *

(c) Total trihalomethanes (the sum of the concentration of bromodichloromethane, dibromochloromethane, tribromomethane [bromoform] and trichloromethane [chloroform]) 0.10 mg/L.

4. By revising the title, the introductory text of paragraph (a) and paragraph (b) of § 141.24 to read as follows:

§ 141.24 Organic chemicals other than total trihalomethanes, sampling, and analytical requirements.

(a) An analysis of substances for the purpose of determining compliance with § 141.12(a) and § 141.12(b) shall be made as follows:

(b) If the result of an analysis made pursuant to paragraph (a) of this section indicates that the level of any contaminant listed in § 141.24 (a) and (b) exceeds the maximum contaminant level, the supplier of water shall report to the State within 7 days and initiate three additional analyses within one month.

5. By adding a new § 141.30 to read as follows:

§ 141.30 Total trihalomethanes sampling, analytical and other requirements.

(a) Community water systems which serve a population of 10,000 or more individuals and which add a disinfectant (oxidant) to the water in any part of the drinking water treatment process shall analyze for total trihalomethanes in accordance with this section. For systems serving 75,000 or more individuals, sampling and analyses shall begin not later than 1 year after the date of promulgation of this regulation. For systems serving 10,000 to 74,999 individuals, sampling and analyses shall begin not later than 3 years after the date of promulgation of this regulation. For the purpose of this section, the minimum number of samples required to be taken by the system shall be based on the number of treatment plants used by the system, except that multiple wells drawing raw water from a single aquifer may, with the State approval, be considered one treatment plant for determining the minimum number of samples. All samples taken within an established frequency shall be collected within a 24-hour period.

(b)(1) For all community water systems utilizing surface water sources in whole or in part, and for all community water systems utilizing only ground water sources that have not been determined by the State to qualify for the monitoring requirements of paragraph (c) of this section, analyses for total trihalomethanes shall be performed at quarterly intervals on at least four water samples for each treatment plant used by the system. At least 25 percent of the samples shall be taken at locations within the distribution system reflecting the maximum residence time of the water in the system. The remaining 75 percent shall be taken at representative locations in the distribution system, taking into account number of persons served, different sources of water and different treatment methods employed. The results of all analyses per quarter shall be arithmetically averaged and reported to the State within 30 days of the system's receipt of such results. Results shall also be reported to EPA until such monitoring requirements have been adopted by the State. All samples collected shall be used in the computation of the average, unless the analytical results are invalidated for technical reasons. Sampling and analyses shall be conducted in accordance with the methods listed in paragraph (e) of this section.

(2) Upon the written request of a community water system, the monitoring frequency required by paragraph (b)(1) of this section may be reduced by the State to a minimum of one sample analyzed for TTHMs per quarter taken at a point in the distribution system reflecting the maximum residence time of the water in the system, upon a written determination by the State that the data from at least 1 year of monitoring in accordance with paragraph (b)(1) of this section and local conditions demonstrate that total trihalomethane concentrations will be consistently below the maximum contaminant level.

(3) If at any time during which the reduced monitoring frequency prescribed under this paragraph applies, the results from any analysis exceed 0.10 mg/L of TTHMs

and such results are confirmed by at least one check sample taken promptly after such results are received, or if the system makes any significant change to its source of water or treatment program, the system shall immediately begin monitoring in accordance with the requirements of paragraph (b)(1) of this section, which monitoring shall continue for at least 1 year before the frequency may be reduced again. At the option of the State, a system's monitoring frequency may and should be increased above the minimum in those cases where it is necessary to detect variations of TTHM levels within the distribution system.

(c)(1) Upon written request to the State, a community water system utilizing only ground water sources may seek to have the monitoring frequency required by subparagraph (1) of paragraph (b) of this section reduced to a minimum of one sample for maximum TTHM potential per year for each treatment plant used by the system taken at a point in the distribution system reflecting maximum residence time of the water in the system. The system shall submit to the State the results of at least one sample analyzed for maximum TTHM potential for each treatment plant used by the system taken at a point in the distribution system reflecting maximum residence time of the water in the system. The system's monitoring frequency may only be reduced upon a written determination by the State that, based upon the data submitted by the system, the system has a maximum TTHM potential of less than 0.10 mg/L and that, based upon an assessment of the local conditions of the system, the system is not likely to approach or exceed the maximum contaminant level for total TTHMs. The results of all analyses shall be reported to the State within 30 days of the system's receipt of such results. Results shall also be reported to EPA until such monitoring requirements have been adopted by the State. All samples collected shall be used for determining whether the system must comply with the monitoring requirements of paragraph (b) of this section, unless the analytical results are invalidated for technical reasons. Sampling and analyses shall be conducted in accordance with the methods listed in paragraph (e) of this section.

(2) If at any time during which the reduced monitoring frequency prescribed under paragraph (c)(1) of this section applies, the results from any analysis taken by the system for maximum TTHM potential are equal to or greater than 0.10 mg/L, and such results are confirmed by at least one check sample taken promptly after such results are received, the system shall immediately begin monitoring in accordance with the requirements of paragraph (b) of this section and such monitoring shall continue for at least one year before the frequency may be reduced again. In the event of any significant change to the system's raw water or treatment program, the system shall immediately analyze an additional sample for maximum TTHM potential taken at a point in the distribution system reflecting maximum residence time of the water in the system for the purpose of determining whether the system must comply with the monitoring requirements of paragraph (b) of this section. At the option of the State, monitoring frequencies may and should be increased above the minimum in those cases where this is necessary to detect variation of TTHM levels within the distribution system.

(d) Compliance with § 141.12(c) shall be determined based on a running annual average of quarterly samples collected by the system as prescribed in subparagraphs (1) or (2) of paragraph (b) of this section. If the average of samples covering any 12 month period exceeds the Maximum Contaminant Level, the supplier of water shall report to the State pursuant to § 141.31 and notify the public pursuant to § 141.32. Monitoring after public notification shall be at a frequency designated by the State and shall continue until a monitoring schedule as a condition to a variance, exemption or enforcement action shall become effective.

(e) Sampling and analyses made pursuant to this section shall be conducted by one of the following EPA approved methods:

(1) "The Analysis of Trihalomethanes in Drinking Waters by the Purge and Trap Method," Method 501.1, EMSL, EPA Cincinnati, Ohio.

(2) "The Analysis of Trihalomethanes in Drinking Water by Liquid/Liquid Extraction," Method 501.2, EMSL, EPA Cincinnati, Ohio.

Samples for TTHM shall be dechlorinated upon collection to prevent further production of Trihalomethanes, according to the procedures described in the above two methods. Samples for maximum TTHM potential should not be dechlorinated, and should be held for seven days at 25° C (or above), prior to analysis, according to the procedres described in the above two methods.

(f) Before a community water system makes any significant modifications to its existing treatment process for the purposes of achieving compliance with § 141.12(c), such system must submit and obtain State approval of a detailed plan setting forth its proposed modification and those safeguards that it will implement to ensure that the bacteriological quality of the drinking water served by such system will not be adversely affected by such modification. Each system shall comply with the provisions set forth in the State-approved plan. At a minimum, a State approved plan shall require the system modifying its disinfection practice to:

(1) Evaluate the water system for sanitary defects and evaluate the source water for biological quality;

(2) Evaluate its existing treatment practices and consider improvements that will minimize disinfectant demand and optimize finished water quality throughout the distribution system;

(3) Provide baseline water quality survey data of the distribution system. Such data should include the results from monitoring for coliform and fecal coliform bacteria, fecal streptococci, standard plate counts at 35° C and 20° C, phosphate, ammonia nitrogen and total organic carbon. Virus studies should be required where source waters are heavily contaminated with sewage effluent;

(4) Conduct additional monitoring to assure continued maintenance of optimal biological quality in finished water, for example, when chloramines are introduced as disinfectants or when pre-chlorination is being discontinued. Additional monitoring should also be required by the State for chlorate, chlorite and chlorine dioxide when chlorine dioxide is used. Standard plate count analyses should also be required by the State as appropriate before and after any modifications;

(5) Consider inclusion in the plan of provisions to maintain an active disinfectant residual throughout the distribution system at all times during and after the modification.

This paragraph (f) shall become effective on the date of its promulgation.

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